Journal of the Oceanographical Society of Japan
Vol. 40, pp. 397 to 404, 1984

Contribution of Raman Scattering to Upward Irradiance in the Sea*

Shigehiko Sugihara†, Motoaki Kishino† and Noboru Okami†

Abstract: Measurements of underwater irradiance revealed that the vertical attenuance in upward irradiance for wavelengths above 520 nm decreased with increasing depth, while the attenuance in the remaining wavelength region and also the attenuance in the downward irradiance in the whole wavelength range kept almost constant values. In this paper, it is suggested that the decrease in the attenuance for the upward irradiance above 520 nm can be ascribed to the Raman scattering of water molecules excited by the intense blue-green light in the downward irradiance.

The pure water Raman scattering function at a scattering angle of 90° is measured and the results are used for the theoretical computation of upward irradiance generated by Raman scattering. Then, the difference between observed upward irradiance and the upward irradiance obtained by extrapolation from that in the shallow layers is computed under the assumption of constant irradiance attenuance. Since this difference is expected to represent the upward irradiance generated by Raman scattering, its value is compared with the upward irradiance due to Raman scattering obtained by theoretical computation. The similarity between the two upward irradiances so evaluated supports the view that Raman scattering makes a significant contribution to upward irradiance in the longer wavelength region.

1. Introduction

Vertical attenuance in underwater irradiance varies, in general, with depth. This is due to the fact that materials such as suspended particles and yellow substance are not uniformly distributed with depth and also that the radiance due to the light scattered from the direct sunlight attains a maximum at a certain depth in the upper layer of the sea. In the lower layer, however, the variation in the irradiance attenuance with depth usually becomes very small; the irradiance on a logarithmic scale shows almost a linear decrease with depth. In fact, most of the results of our recent downward irradiance measurements in oceanic water showed that the attenuance becomes constant with depth in the lower layer. The attenuance of upward irradiance, however, decreased even in the lower layer in the yellow region of the spectrum as the depth increased.

In this paper, it will be shown that the decrease in the attenuance for the upward irradiance in the yellow region of the spectrum can be attributed to the contribution of Raman scattering of water molecules excited by the downward propagating blue-green light.

Spectral downward and upward irradiance data used in this study were collected in Sagami Bay on 23 and 26 May 1982, during the R/V *Tansei Maru* cruise KT-82-5, using an irradiance meter which can measure the downward and upward irradiances simultaneously. A detailed description of this meter has already been given by Kishino and Okami (1984). The locations of the stations at which irradiance measurements were carried out are shown in Fig. 1.

2. Attenuance in downward and upward irradiances

Figure 2 shows the vertical profiles of downward and upward irradiances on a logarithmic scale observed at Station 28. At almost all the wavelengths selected in the figure, the downward irradiance decreases linearly with increasing depth below 30 m. Further, the attenuance in the upward irradiance at all the wavelengths except 600 nm and 650 nm also seems to follow

---

* Received 1 May 1984; in revised form 7 July 1984; accepted 23 July 1984.

† The Institute of Physical and Chemical Research, Hirosawa 2-1, Wako, Saitama 351-01, Japan

a linear decrease from 6.0 m to 50 m. The decrease in irradiance at 650 nm can be ascribed to the fluorescence of phytoplankton pigments (Kishino *et al.*, 1984). Below 50 m, however, the attenuance for the upward irradiance shows a slight decrease at the wavelength of 580 nm. As will be shown below the considerable decrease in attenuance in the upward irradiance between 68.2 m and 83.8 m can be ascribed to the influence of sea floor reflection.

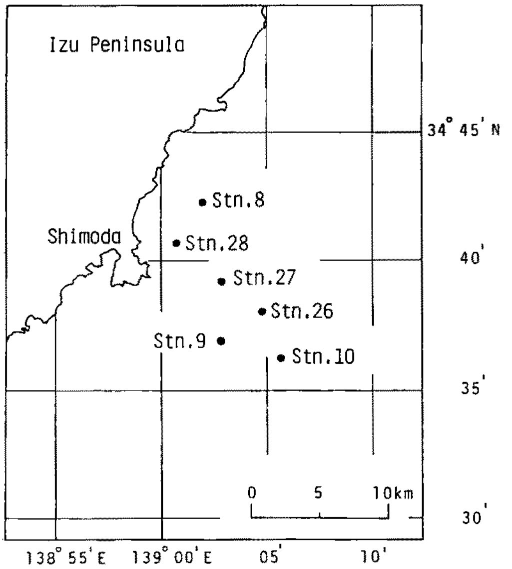


Fig. 1. The locations of the stations where irradiance was measured during the R/V *Tansei Maru* cruise KT-82-5.

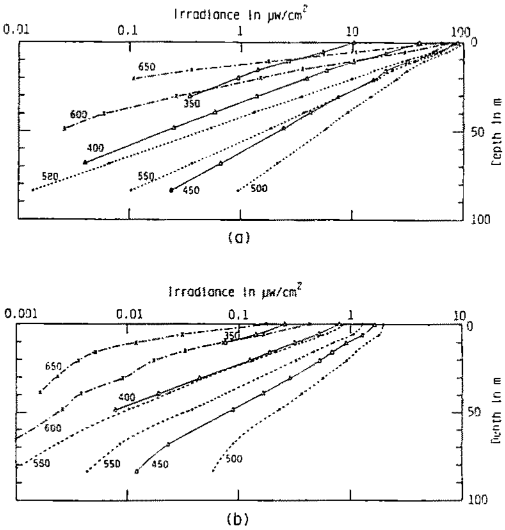
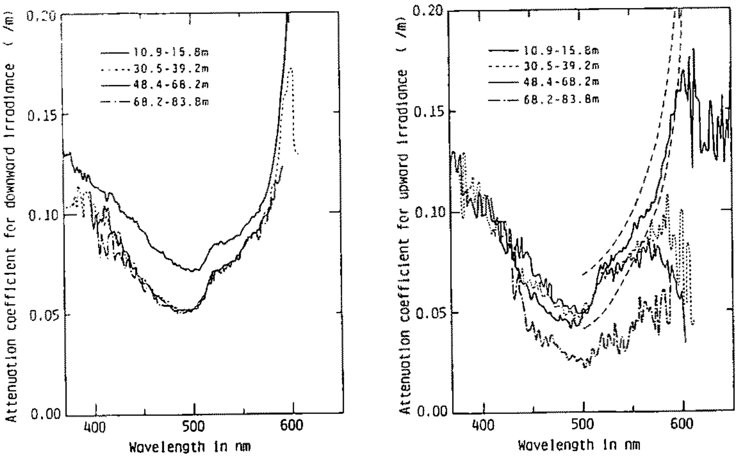


Fig. 2. Vertical profiles of irradiance observed at Station 28. (a) Downward irradiance. (b) Upward irradiance. Numerals next to curves indicate wavelength (nm).



(a) (b)

Fig. 3. Spectral attenuation coefficient for downward (a) and upward (b) irradiance in four layers: 10.9 m-15.8 m, 30.5 m-39.2 m, 48.4 m-68.2 m and 68.2 m-83.8 m, at Station 28. The two broken curves above 500 nm, represent attenuation coefficients for downward irradiances for oceanic water types IB (lower curve) and II (upper curve) from Jerlov (1968).

The decrease in the attenuance for the upward irradiance with depth is more clearly recognized in the spectral irradiance attenuation coefficient. In Fig. 3, for example, the attenuation coefficients for downward irradiance, K_d, and upward irradiance, K_u, in four of the layers are plotted as a function of wavelength. At each wavelength below 500 nm, K_d in the lower three layers (30.5 m–39.2 m, 48.4 m–68.2 m, and 68.2 m–83.8 m) is almost equal to K_u in the upper three layers (10.9 m–15.8 m, 30.5 m–39.2 m, and 48.4 m–68.2 m). In the longer wavelength region, however, K_u becomes smaller than K_d. A smaller K_u in this region is also recognized by comparison with K_d given by Jerlov (1968). Broken curves above 500 nm in Fig. 3(b) represent his values of K_d for the oceanic water types IB (lower) and II (upper) which he classified optically. With increasing depth, the discrepancy between K_d and K_u becomes larger. The wavelength at which K_u becomes smaller than K_d is about 600 nm in the 10.9–15.8 m layer and about 520 nm in both the 30.5–39.2 m and 48.4–68.2 m layers. It is noticeable that some K_u are smaller than the attenuation coefficient of pure water. For example, K_u at 580 nm in the layers 30.5–39.2 m and 48.4–68.2 m is smaller than 0.08 m^{-1} while the pure water attenuation coefficient reported by Sullivan (1963) is 0.109m^{-1} at this wavelength. Since the scattering coefficient given by Morel (1974) is about 0.00125 m^{-1}, the absorption coefficient of pure water is about 0.108 m^{-1} at 580 nm. Accordingly, K_u in these two layers is smaller than even the absorption coefficient of pure water. As shown in Fig. 4, a smaller K_u in the yellow region of the spectrum is also observed at all of the stations where irradiance was measured.

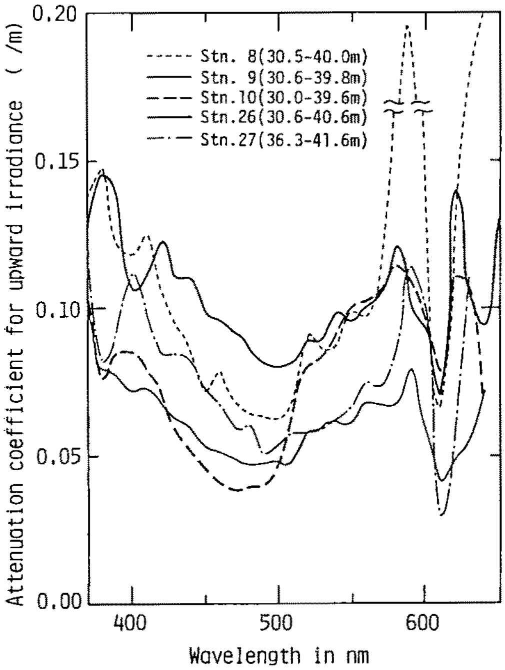


Fig. 4. Spectral attenuation coefficient for upward irradiance at each station.

Since the vertical variation of K_u is small at wavelengths below 500 nm and their values are almost equal to K_d in the lower three layers, the vertical variation of the concentration of suspended materials and yellow substance can be considered to be small. Accordingly, the smaller K_u in the yellow region of the spectrum suggests the production of light which contributes to the upward irradiance.

One of the possible processes producing the additional light is the fluorescence of materials such as chlorophyll and the yellow substance present in sea water. However, the fluorescence emission spectrum of chlorophyll *a in vivo* has a sharp peak with a width of about 25 nm near 685 nm (Kishino *et al.*, 1984). Therefore, we can consider that the contribution of chlorophyll *a* fluorescence to the upward irradiance is negligible in the wavelength region below 600 nm. In addition to this, the reported emission spectra of sea water or dissolved organic materials show that maximum emission occurs below at least 500 nm and the emission is weak in the yellow region of the spectrum (Kalle, 1937; Shapiro, 1957; Traganza, 1969; Brown, 1974). Accordingly, the decrease in the attenuance for the upward irradiance in the yellow region cannot be explained by the fluorescence of chlorophyll *a* and yellow substance.

Since the water depth at Station 28 is 84 m, the effect of sea floor reflection on the upward irradiance must be considered. Joseph (1950), and also Plass and Kattawar (1972) showed a decrease in the attenuance of irradiance near the sea floor. If the floor is not so strongly colored, the light reflected by the floor affects the upward irradiance for the whole region of the spectrum non-selectively. As shown in Fig. 3, this situation is found in K_u in the layer between 68.2 m and 83.8 m. In the whole visible region of the spectrum, K_u is about half of that for the upper three layers, but the shape of the curve of K_u is similar to that of K_u in the layer between 10.9 m and 15.8 m. Further, K_d in the same layer keeps almost the same levels as those for the upper three layers, as is also shown in Fig. 3. These facts suggest that K_u in the layer between 63.2 m and 83.8 m is affected by sea floor reflection. The reason why only K_d keeps the same levels is due to the fact that the downward irradiance is little affected by the sea floor because reflected light must be scattered downwards before it can reach the detector. On the other hand, K_u differs only slightly for the upper three layers in the wavelength region below 500 nm and also K_u for the upper three layers is almost equal to K_d at each wavelength below 500 nm. Therefore, we can consider that the sea floor effect is negligible for the upper three layers.

Now let us consider Raman scattering of water molecules excited by very intense downward blue-green light. There are grounds for believing that some fractions of light in the upward irradiance are produced by such scattering, and the experimental evidence for this can be summarized as follows:

(i) Occurrence of K_u smaller than K_d is limited to wavelengths above 520 nm and also to the deep layers.

(ii) The difference between K_u and K_d increases with increase of both wavelength and depth.

(iii) In the wavelength region between 520 nm and 600 nm where K_u is smaller than K_d, the fluorescence of materials present in the sea water is too weak to contribute greatly to the upward irradiance.

(iv) Judging from the spectral distribution of downward irradiance, the Raman spectrum is expected to be present in the yellow-green region where K_u is smaller than K_d.

(v) The relative intensity of the blue-green light, which excites the water molecules and generates Raman scattering in the yellow region of the spectrum, is very large while the relative intensity of upward irradiance is very small in the yellow region.

As stated above, K_u in the layer between 68.2 m and 83.8 m is very small, because the downward flux is reflected by the sea floor and some of this reflected fraction can contribute to upward irradiance (E_u) at 83.8 m. In this case, E_u that is produced through the process of ordinary scattering and also by the Raman scattering becomes small because the light path between the detector and the sea floor becomes short. This explains why the spectral shape of K_u is similar to that of K_d near the sea floor, even above 500 nm.

It should be noted here that the Raman scattering flux can only be detected in the upward light field because of the low level of the light field while it remains undetected in the high level light field of the downward flux.

3. Raman intensity at a scattering angle of 90°

In order to estimate the contribution of Raman scattering to the upward irradiance, we need to know the volume Raman scattering function of water molecules. The Raman cross section of water at 488 nm was measured by Slusher and Derr (1975). However, spectral dependence of Raman scattering has not yet been determined experimentally. The Raman scattering function β at 90° for distilled water was measured with a Hitachi fluorometer (Fluorescence spectrophotometer Model 650). The spectral sensitivity of the detector was standardized by comparing it with a reference light emitted from a white diffuser irradiated by an NBS standard lamp. In order to eliminate the ultraviolet light, two glass plates 1 mm thick were placed between the sample cell and the emission monochromator. The distilled water was irradiated by the monochromatic light at seven wavelengths λ_0 between 400 nm and 550 nm at intervals of 25 nm. The half band width of excitation wavelength was 5 nm for every λ_0. With the wavelength set on the excitation monochromator, the remainder of the wavelength ($>\lambda_0$) was scanned automatically. Output from the detector of the photomultiplier tube was fed to an x-y recorder.

Figure 5 shows the observed Raman spectra of distilled water, when it is excited by monochromatic light of various wavelengths. As the wavelength of the light λ_0 increases, the maximum intensity of the Raman spectrum decreases but the band width increases. From the experimental data obtained here, we see that the relation between λ_0 and the wavelength with

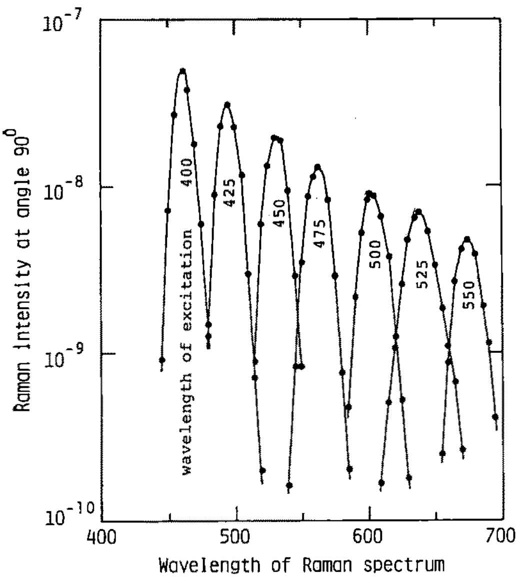


Fig. 5. Raman spectra when water molecules are excited by monochromatic light of various wavelengths. Numerals beneath curves indicate wavelength of excitation (nm).

maximum intensity in the Raman spectrum (λ_{max}) can be approximated as

$$\lambda_{max}(\lambda_0)=\frac{\lambda_0}{-3357\cdot 10^{-7}\cdot\lambda_0+1}. \quad (1)$$

Since the shape of each Raman spectrum can be represented by a Gaussian function, β, at the emission wavelength λ is expressed by

$$\beta(\lambda_0,\lambda,\pi/2)$$
$$=A(\lambda_0)\cdot\exp\left[-\left\{\frac{\lambda-\lambda_{max}(\lambda_0)}{\sigma(\lambda_0)}\right\}^2\right], \quad (2)$$

where A is the maximum intensity which occurs at λ_{max}, and σ is the standard deviation. Integration of Eq. (2) with respect to λ to obtain the total Raman scattering intensity at the scattering angle 90° ($B(\lambda_0)$) gives

$$B(\lambda_0)=A(\lambda_0)\int\exp\left[-\left\{\frac{\lambda-\lambda_{max}(\lambda_0)}{\sigma(\lambda_0)}\right\}^2\right]d\lambda$$
$$=A(\lambda_0)\cdot\sigma(\lambda_0)\cdot\pi^{1/2}. \quad (3)$$

Computed B as a function of λ_{max} is presented in Fig. 6, in which two curves, one indicating a spectral dependence proportional to λ_{max}^{-4} and the other a dependence proportional to λ_{max}^{-5},

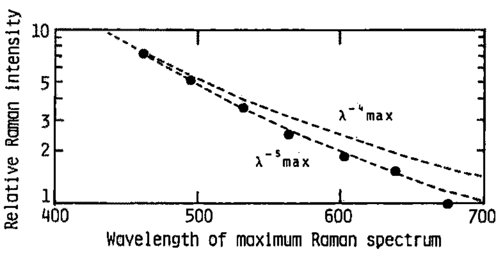


Fig. 6. Total Raman intensity at a scattering angle of 90° as a function of peak wavelength in the Raman spectrum.

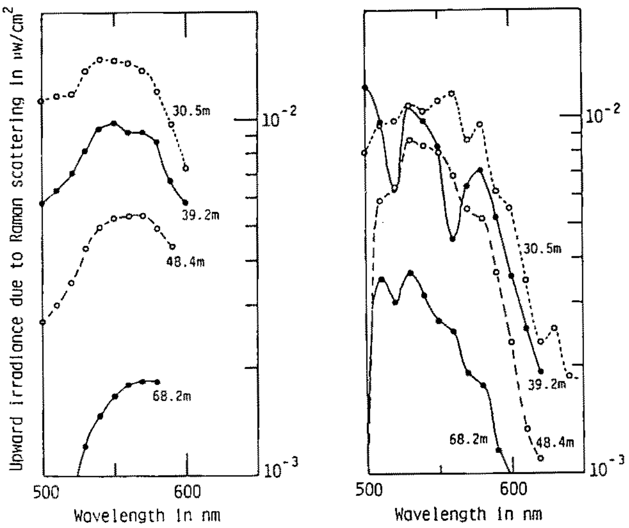
are also presented. Computed B fits the λ_{max}^{-5} rather than the λ_{max}^{-4} curve. The intensity of the Raman spectrum has previously been formulated by Behringer (1967). When the denominator of α in his Eq. (8) is not small, the intensity should vary as the inverse fourth power of the output frequency. The reason why the Raman spectrum intensity obtained deviates from λ_0^{-4} dependence is not clear. However, the deviation of spectral dependence of B from λ_{max}^{-4} suggests that the denominator of α is smaller at shorter wavelengths.

In order to obtain the Raman intensity in absolute units, the volume scattering function of pure benzene at 90° was used as a standard. The volume scattering function of pure benzene at 90° was reported by Cantow (1956). The conversion factor to absolute units obtained from his scattering function was divided by the square of the ratio of the refractive index of water to that of benzene, in order to take account of the difference in refractive index between water and benzene.

The value of B at 488 nm obtained by interpolation from B observed at 475 nm and 500 nm was 0.000067 m^{-1} str^{-1}. An experimentally measured value of 4.5×10^{-33} m^2 $molecule^{-1}$ str^{-1} for the Raman cross section of water was reported by Slusher and Derr (1975). Their value is equivalent to a volume scattering function of 0.00015 m^{-1} str^{-1}, which is about two times larger than the result obtained here. One of the reasons for the discrepancy is that the excitation light used by Slusher and Derr was polarized whereas we used unpolarized light.

4. Contribution of Raman scattering to upward irradiance

Upward irradiance produced by E_d through



(a) (b)

Fig. 7. (a) Evaluated upward irradiance due to the Raman scattering at three depths by means of the single scattering model. (b) The difference between observed E_u and E_u evaluated from E_u in shallow layers assuming an exponential decrease down to the deeper layers.

the process of Raman scattering is roughly evaluated on the basis of the single scattering model presented by Jerlov and Fukuda (1960).

With increasing depth from z to z' $(z'>z)$, the downward irradiance decreases from E_z to $E_{z'}$ as

$$E_{z'}(\lambda_0)=E_z(\lambda_0)\cdot\exp\left[-K_d(\lambda_0)\cdot\{z'-z\}\right], \quad (4)$$

where K_d is the attenuation coefficient for downward irradiance. The intensity scattered in the direction of (θ,ϕ) by the Raman effect of water molecules in a small volume element at z' produces radiance which will be written as L at z which is at a distance of r from the element at z'. If the Raman scattering is assumed to be isotropic, then L due to primary scattering is expressed by

$$L(\theta,\lambda_0,\lambda)=\beta(\lambda_0,\lambda)\int_0^\infty E_{z'}(\lambda_0)\exp\{-c(\lambda)\cdot r\}dr$$

$$=\frac{\beta(\lambda_0,\lambda)\cdot E_z(\lambda_0)}{c(\lambda)-K_d(\lambda_0)\cos\theta}. \quad (5)$$

Accordingly, the upward irradiance produced by Raman scattering, $dE_R(\lambda_0)$, is given by

$$dE_R(\lambda_0,\lambda)=\int_0^{2\pi}\int_{\pi/2}^{\pi}L(\theta,\lambda_0,\lambda)|\cos\theta|\sin\theta\, d\theta\, d\phi$$

$$=2\pi E_z(\lambda_0)\frac{\beta(\lambda_0,\lambda)}{K_d(\lambda_0)^2}\left[K_d(\lambda_0)+c(\lambda)\cdot\log\frac{c(\lambda)}{K_d(\lambda_0)+c(\lambda)}\right]. \quad (6)$$

The total upward irradiance produced by Raman scattering (E_R) is derived by integration of Eq. (6) with respect to λ_0. For this purpose, c must be known. For simplicity, c in Eq. (6) was assumed to be equal to K_d at λ. Thus, Eq. (6) could be solved. The results of computation are shown in Fig. 7(a).

At the depth of 30.5 m, the computed upward irradiance generated by Raman scattering peaks in the vicinity of 550 nm. With increasing depth, the peak shifts toward longer wavelengths; the peak is found at around 575 nm at 68.2 m. The shift of the peak corresponds to the spectral change in E_d which shows a relative decrease in the shorter wavelength region with increasing depth.

On the other hand, the upward irradiance due to Raman scattering can also be evaluated from the observed upward irradiance as follows. The upward irradiance in the layer between 6.0 m and 15.8 m shows a linear decrease on the semilogarithmic plot with increasing depth. If the upward irradiance continues to decrease linearly with depth below this level, then the upward irradiance in the absence of Raman scattering can be obtained in the deeper layers by extrapolation. Accordingly, the difference between the observed upward irradiance and the extrapolated irradiance should give a measure of the upward irradiance produced by Raman scattering (denoted by ΔE_u). In order to reduce the oscillatory variation of ΔE_u with wavelength, ΔE_u was smoothed by taking a running mean, as plotted in Fig. 7(b). The oscillatory variation is due to an inaccuracy in the computed K_u's which have a large effect on the computed values of E_u. The shapes and the magnitude of E_R and ΔE_u are generally similar.

The general agreement between the two different calculations of upward irradiance due to Raman scattering supports the view that Raman scattering is responsible for K_u being smaller than K_d in the yellow region of the spectrum in the deep layers.

Acknowledgements

We would like to thank Dr. Y. Fujita, National Institute for Basic Biology, Dr. M. Takahashi, University of Tsukuba, participants of the KT-82-5 cruise and the crew of the *Tansei Maru*, Ocean Research Institute, University of Tokyo, for their kind help and encouragement during the cruise.

We are also grateful for the kind encouragement and advice given by Dr. S. Unoki, the Institute of Physical and Chemical Research.

References

Behringer, J. (1967): Observed resonance Raman spectra. In: Raman Spectroscopy, Theory and Practice, ed. by H.A. Szymanski, Plenum Press Inc., New York, pp. 168-223.

Brown, M. (1974): Laboratory measurements of fluorescence spectra of Baltic waters. Univ. Copenhagen, Inst. Phys. Oceanogr. Rep., **29**, 1-31.

Cantow, H. J. (1956): Rayleigh-Konstanten reiner Lösungsmittel und ihre Wellenlängenabhängigkeit. Makromol. Chem., **18/19**, 367-374.

Jerlov, N.G. (1968): Optical oceanography. Elsevier, Amsterdam, 194 pp.

Jerlov, N.G. and M. Fukuda (1960): Radiance distribution in the upper layers of the sea. Tellus, **12**, 348-355.

Joseph, J. (1950): Untersuchungen über Ober- und Unterlichtmessungen im Meere und über ihren Zusammenhang mit Durchsichtigkeitsmessungen. Dtsch. Hydrogr., **3**, 324-335.

Kalle, K. (1937): Meereskundliche chemische Untersuchungen mit Hilfe des Zeisschen Pulfrich-Photometers. VI, Mitt. Die Bestmmung des Nitrats u.d, Gelbstoffes. Ann. Hydrogr., **65**, 276-282.

Kishino, M. and N. Okami (1984): Instrument for measuring downward and upward spectral irradiances in the sea. La mer, **22**, 37-40.

Kishino, M., S. Sugihara and N. Okami (1984): Influence of fluorescence of chlorophyll *a* on underwater upward irradiance spectrum. La mer, **22**. 224-232.

Morel, A. (1974): Optical properties of pure water and pure sea water. In: Optical Aspects of Oceanography, ed. by N. G. Jerlov and E. Steeman-Nielsen, Academic Press, London and New York, pp. 1-24.

Plass, G.N. and G.W. Kattawar (1972): Monte Carlo calculations of radiative transfer in the earth's atmosphere-ocean system I. Flux in the atmosphere and ocean. J. Phys. Oceanogr., **2**, 139-145.

Shapiro, J. (1957): Chemical and biological studies on the yellow organic acids of lake water. Limnol. Oceanogr., **2**, 161-179.

Slusher, R. B. and V. E. Derr (1975): Temperature dependence and cross sections of some Stokes and anti-Stokes Raman lines in ice Ih. Appl. Opt., **14**, 2116-2120.

Sullivan, S.A. (1963): Experimental study of the absorption in distilled water, artificial sea water, and heavy water in the visible region of the spectrum. J. Opt. Soc. Am., **53**, 962-968.

Traganza, E.D. (1969): Fluorescence excitation and emission spectra of dissolved organic matter in sea water. Bull. Mar. Sci. Univ. Miami, **19**, 897-904.

海中ラマン散乱光の照度に及ぼす影響

杉原滋彦*，岸野元彰*，岡見　登*

要旨: 海中照度は深さの増大と共に減衰し，その減衰率は波長に依存するが，一定波長の下では，表層近くを除きほぼ一定の値を示すのが一般的な傾向である．しかし，相模灘で実測した天頂方向照度(Ed)の減衰率がほぼ一定であるのに対し，天底方向照度(Eu)の減衰率は，深さの増大と共に波長 520 nm 以上に於て減少する傾向が認められる．この減衰率の減少は従来の散乱と吸収の理論からは説明出来ず，何らかの要因で新たな光が生産されている事を示唆する．波長 685 nm 付近では，クロロフィル*a*による蛍光の影響のため，照度の減衰率が減少する事が考えられるが，波長 520 nm から 650 nm の間における減少をクロロフィル*a*の蛍光では説明出来ない．またこの波長域では溶存物質による蛍光の小さい事を考えると，波長 500 nm 付近に最大値を有し，かつ Eu に比べはるかに強い Ed によって励起された海水分子のラマン散乱光の影響を考えざるを得ない．そこで純水のラマン散乱光強度を測定し，この結果を使って海中一次ラマン散乱光による天底方向照度を計算した．一方，実測した天底照度が深層まで一定の割合で減衰することを仮定し，深層における天底照度を求めた．こうして求めた照度と実測照度の差がラマンスペクトルの大きさを表わすものと考え，計算した一次ラマン散乱光照度と比較した．両者は全体の形状や強度に一致が見られ，天底方向照度にラマン散乱光が影響を与えるという仮定を支持する．

---

* 理化学研究所　〒351-01　和光市広沢 2-1