

Remote sensing of subsurface water temperature by Raman scattering

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The application of Raman scattering to remote sensing of subsurface water temperature and salinity is considered, and both theoretical and experimental aspects of the technique are discussed. Recent experimental field measurements obtained in coastal waters and on a trans-Atlantic/Mediterranean research cruise are correlated with theoretical expectations. It is concluded that the Raman technique for remote sensing of subsurface water temperature has been brought from theoretical and laboratory stages to the point where practical utilization can now be developed.

I. Introduction

The rapidly increasing concern for improving man's understanding of the ocean requires and justifies an immediate acceleration in attempts to measure and monitor its significant properties. Basic among such ocean properties is the global thermal structure of the ocean in the first 100 m of depth. The ability to measure optically by remote methods the subsurface temperature profile of the ocean is the subject of this paper.

There currently exists no known capability to measure remotely subsurface ocean temperature profiles. A remote, wide area coverage, airborne or satellite measuring device capable of surface penetration and temperature measurement to ocean depths of the order of 100 m would provide for weather and climate prediction valuable and complementary information to the ocean surface temperature data that are now currently available. Such a remote subsurface temperature measurement capability would also benefit other research and technology areas such as sea-air interaction modeling, the physics of oceanic mesoscale systems, behavior of ocean fronts and other mixed layer ocean dynamics, the synoptic behavior of acoustic propagation in the ocean, and the monitoring and validation of models for thermal discharges into water bodies relevant to the operation of conventional fossil fuel and nuclear power plants and for ocean thermal energy conversion (OTEC) power plants.

In this paper we report experimental remote sensing of subsurface water temperature using the Raman technique. The physical basis of the measurement can be described by the following: (a) liquid water exists in at least two forms, monomer and polymer; (b) the two forms are in chemical equilibrium as a function of temperature; (c) the O—H Raman stretching frequency is significantly different for the monomer and polymer forms; (d) the relative concentration of monomer vs polymer can be determined from the Raman spectrum, and thus the temperature can be inferred.

This model is shown in a heuristic manner by means of the Raman spectrum in Fig. 1. Liquid water is considered as being composed of two species, polymers which are hydrogen bonded and monomers which are not, both in rapid equilibrium with each other as a function of temperature. Each species has its individual Raman spectrum proportional to its concentration as shown in the schematic, the total observed Raman spectrum being composed of the sum. Simultaneous measurement of the Raman spectra at the two wavelengths λ_1 and λ_2 provides a measure of the concentration ratio and through an equilibrium constant the temperature. Such a two-species mixture model of liquid water has previously been successfully used in interpreting sound absorption measurements¹ and in infrared^{2,3} and Raman spectroscopic studies.⁴

Our investigations were aimed at bringing the Raman technique from the theoretical and laboratory stages to the point where field experiments could be used to validate the concept for practical remote sensing utilization. We have obtained highly resolved experimental Raman spectra of subsurface ocean water from two research vessels in both coastal and open ocean waters. These experimental results strongly support our design calculations which showed that Raman spectra can be used for remote sensing of subsurface ocean tempera-

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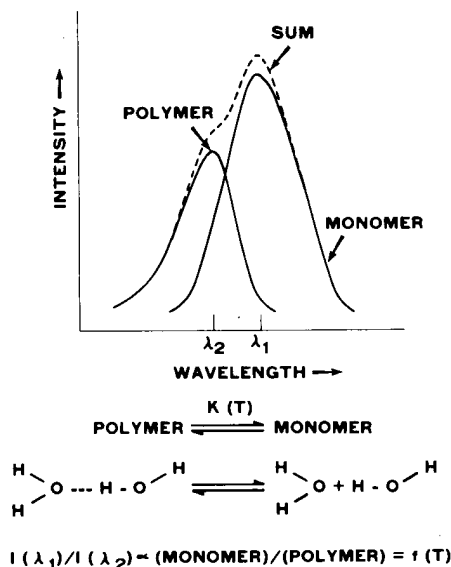


Fig. 1. Raman spectrum and structure of liquid water.

ture profiles. Interferences, including surface wave effects, volume differential attenuation, volume differential depolarization, and non-Raman photon noise sources such as ambient sunlight and laser-induced fluorescence are also considered.

II. Background

The prior research activities upon which the current work is based fall into four general categories: (1) laboratory measurements of the temperature and salinity dependence of the Raman spectra of liquid water; (2) remote laser Raman atmospheric field experiments; (3) airborne oceanographic lidar measurements for bathymetry and oil slick detection purposes; and (4) a limited number of laser Raman measurements of subsurface water temperature in New England coastal waters.

A. Laboratory Experiments

Walrafen⁵ at Bell Telephone Laboratories was one of the first to observe experimentally in the 1960s that the laser Raman spectrum of liquid water in the perturbed O—H stretch region (2800–3900 cm⁻¹) shifts toward longer wavelengths with increasing temperature. Walrafen's work showed that by monitoring the Raman spectra of liquid water in the O—H region, the variation of molecular structure due to the mobility of the hydrogen bonds may be observed, and the shape of the Raman spectra, therefore, provides a means for measuring the temperature of liquid water.

Polarization spectroscopy may also be used to study the Raman spectrum of liquid water. Using this technique the water sample is illuminated with a polarized laser beam. Two Raman spectra are recorded, one in the same polarization as the laser beam, the other in the orthogonal polarization. The ratio of the two polarization spectra, when computed as a function of wave-

length, is found also to be temperature dependent.⁶ Polarization spectroscopy has unique advantages for deep penetration applications, which will be discussed later in the paper.

Schwiesow⁷ in 1971 first suggested and conducted experiments to show that the Raman techniques could be employed for remote water temperature measurements. More recently, Chang *et al.*⁸ demonstrated the feasibility of the method as a remote temperature sensor in a series of laboratory experiments, which investigated both a two-color technique and a depolarization technique. The basic sensitivity of the measurement was shown to be about 1% per °C, and it was estimated that the expected performance of an airborne system would be a temperature determination accuracy of 0.5 °C at a depth of four diffuse attenuation lengths per joule of laser energy transmitted. The effect of salinity was also experimentally investigated and was shown to be separable from temperature using polarization techniques with a sensitivity of about 1% per 3 parts per 10³ concentration change.

An experimentally measured value of 4.5×10^{-33} m²/molecule-sr for the liquid O—H stretching band Raman cross section has been reported by Slusher and Derr.⁹ Table I shows a representative, but by no means complete, compilation of volume backscattering coefficients that have been measured by various investigators for distilled water and ocean and lake water of various types. Also included in Table I are Raman backscattering coefficients for distilled water and ice. The wavelength of light used for the measurements cited in Table I varies somewhat from investigator to

Table I. Comparison of Raman and Volume Scattering Coefficients for Water

Raman scattering coefficient ($\lambda = 488 \text{ nm}$) ($\text{m}^{-1}/\text{sr}^{-1}$)		
Distilled water	0.00015	Slusher and Derr (1975) ^a
Ice	0.000093	Slusher and Derr (1975) ^a
Volume on-frequency scattering coefficient, σ (180°) ($\text{m}^{-1} \text{sr}^{-1}$)		
Distilled water	0.00017–0.00020	Tyler (1961) ^b
Ocean		
Various locations, eastern North Atlantic	0.0005	Jerlov (1961) ^c
Off Bermuda (31°57'N, 65°11'W)	0.002	Morrison (1970) ^d
Coastal		
Between Woods Hole and the 180-m contour	0.003–0.004	Sphilhaus (1968) ^e
Near Santa Catalina Island (33°32'N, 118°17'W)	0.00020	Tyler (1961) ^b
Long Island Sound (41°16'N, 70°08'W)	0.02	Morrison (1970) ^d
Lake		
Winnepesaukee, New Hampshire	0.003	Duntley (1963) ^f
Pend Oreille, Idaho	0.00017–0.0041	Tyler (1961) ^b

^a See Ref. 9.

^b See Ref. 10.

^c See Ref. 11.

^d See Ref. 12.

^e See Ref. 13.

^f See Ref. 14.

investigator, but all use light in the blue-green near 500 nm so that order-of-magnitude comparisons may be considered valid.

From the data compiled in Table I it can be noted that the Slusher and Derr value for the Raman coefficient is essentially equal to the on-frequency backscatter coefficient of Tyler for distilled water. Far from being a weak effect the Raman return is comparable with the main on-frequency return from the water itself. This has implications when making comparisons between the Raman method and other laser scattering methods for remote subsurface measurements such as the Brillouin technique to determine sound speed.¹⁵

It should also be noted that the cross section for ice is comparable with that of liquid water. Slusher and Derr⁹ have obtained temperature measurements using Stokes to anti-Stokes line ratios in ice from 0°C to -50°C. A Raman instrument capable of measuring liquid water temperature and salinity should, therefore, also be capable of not only detecting the spectral signature of ice but also of measuring ice temperatures.

Laboratory experiments with natural waters were carried out by Zimmerman and Bandy,¹⁶ who conducted laboratory laser-induced scattering measurements with samples taken in estuarine waters near Norfolk, Virginia. While the purpose of their work was not to measure water temperature, the Raman O—H stretch band is sufficiently resolved in the data that they published so that the ratio of monomer to polymer can be determined after subtraction of the fluorescence level to yield a water temperature value in the mid to upper 70s °F (20s °C), which would be typical of a laboratory situation. (Walrafen's data⁵ were used as a calibration.)

B. Remote Raman Field Measurements

The use of laser backscattering in remote sensing field applications began with the 1963 atmospheric experiments of Fiocco and Smullin.¹⁷ This work was extended to include laser Raman atmospheric measurements by Leonard¹⁸ in 1967, who detected N₂ and O₂ in the atmosphere at a distance of 1 km. Subsequent work by Cooney,¹⁹ Melfi *et al.*,²⁰ and Strauch *et al.*²¹ showed that the laser Raman method could be used for quantitative remote measurement of vertical water vapor concentration profiles in the atmosphere.

Laser Raman backscattering has also been employed by Leonard and Caputo²² to measure atmospheric transmission. The measurement of atmospheric temperature by band shape analysis of laser Raman backscatter was demonstrated by Salzman and Cooney.²³ Similar Raman band shape analysis techniques have been employed in combustion diagnostic applications.²⁴

Precision remote laser Raman measurements have thus been demonstrated to be feasible under a variety of field conditions, and this technology is directly applicable to the utilization of laser Raman scattering for subsurface water temperature measurements.

C. Field Experiments With Airborne Oceanographic Lidars

Experimental airborne lidar systems have already been shown to be useful for shallow water bathymetry measurements,^{25,26} the detection and identification of oil slicks,²⁷ and the detection and identification of algae.²⁸ The recent results obtained by the NOAA group²⁶ are important because they demonstrate that depth resolutions in the 10–20-cm range are routinely obtainable with an airborne oceanographic lidar.

Of special interest is the airborne laser oil slick remote sensing experiments that were carried out by Fantasia and Ingrao.²⁷ Laser-induced water Raman spectra, referred to as sea water fluorescence spectra by Fantasia and Ingrao, were routinely monitored in flight tests and were used as a calibration base in the detection of oil spills. Band shape analysis of these spectra is the basis of the Raman subsurface water temperature measurement technique.

D. Coastal Water Measurements

Successful remote Raman measurements of subsurface spectra have previously been reported by Leonard *et al.*²⁹ in experiments conducted in coastal waters of Massachusetts. These preliminary results showed that Raman spectra obtained from natural coastal waters could be analyzed to within ±2°C when compared to ground truth and that accuracies of better than ±1 °C were expected from an improved experimental system in the first one to two optical attenuation lengths of depth.

III. Performance Estimates

The performance of a fully developed Raman lidar subsurface temperature measurement system, if not limited by interferences, can be exactly calculated.

The number of Raman photoelectrons collected per second by an optical detector in a pulsed laser backscattering system can be expressed by the following equation:

$$N_{pe} = N_{laser} N_{scat} \sigma_{Raman} \Delta R \frac{\Omega}{n^2} \epsilon_{pe} \epsilon_{op} T_{\lambda_1} T_{\lambda_2} \quad (1)$$

where N_{pe} = number of Raman photoelectrons detected,
 N_{laser} = number of laser photons transmitted,
 N_{scat} = density of molecular scatters of a given species,
 σ_{Raman} = Raman scattering cross section per particle per steradian,
 ΔR = range resolution,
 Ω = detection solid angle of collector,
 n = refractive index of water,
 ϵ_{pe} = photocathode photoelectric efficiency,
 ϵ_{op} = optical system efficiency, and
 $T_{\lambda_1} T_{\lambda_2}$ = two-way transmission, T_{λ_1} at laser wavelength and T_{λ_2} at Raman wavelength.

Table II. System Parameter Values

System parameter	Value assumed	Rationale
N_{laser}	2.3×10^{17} photons/sec	This value corresponds to 0.1 W of average power at 4600 Å. Commercially available N_2 pumped dye lasers have this capability
$N_{\text{Raman scat}}$	1.5×10^{-4} $\text{sr}^{-1}\text{m}^{-1}$	This is the latest published value for the experimentally measured total Raman liquid water backscatter coefficient ^a
ΔR	1 m	Corresponds to minimum depth resolution set by pulse duration of laser
Ω/n^2	2×10^{-7} sr	This collection solid angle corresponds to a 30-cm effective diam collector on a platform 500 m above the subsurface scattering volume
ϵ_{optpe}	5×10^{-2}	Typical over-all optical and photoelectric quantum efficiency

^a See Ref. 9.

It can be seen from the above that if the transmitter and receiver system parameters are known and if the Raman scatterer has a known cross section and density such as liquid water, a measure of the Raman scattering from a single range cell can be used to determine the two-way transmission to that range cell. The system thus acts as a single-ended transmissometer. The Raman technique for transmission measurements in the atmosphere has already been demonstrated.²²

The subsurface water temperature measurement performance of a typical Raman lidar system was estimated using Eq. (1) with system parameters that assume modest but well-engineered components. The system parameters assumed are listed in Table II, with a brief rationale for the particular choice of the value of each parameter.

The product of the system parameters shown in Table II yields a total Raman signal return of 3.5×10^5 photoelectrons per second with the assumption of unity two-way transmission loss, i.e., surface or near-surface measurements. As has been previously shown,³⁰ in a well-engineered Raman system using a pulsed laser, the limiting noise in the absence of external noise sources can be reduced to the shot noise in the laser-induced Raman signal itself. Therefore, the SNR can be given by the square root of the total number of photoelectrons collected in a given measurement time interval. This SNR assumption has been verified by data obtained in laser Raman field experiments.³⁰ If the signal in the above calculation is assumed to be equally divided between the two polarizations, a basic SNR of $(1.75 \times 10^5)^{1/2}$ or 418 would be available. Based on a measurement sensitivity of 1% per °C, this would mean that a temperature precision of $(1/418) \times 100 \approx 0.2^\circ\text{C}$ would have been achieved.

The ability to achieve depth penetration depends critically on the diffuse attenuation coefficient of the

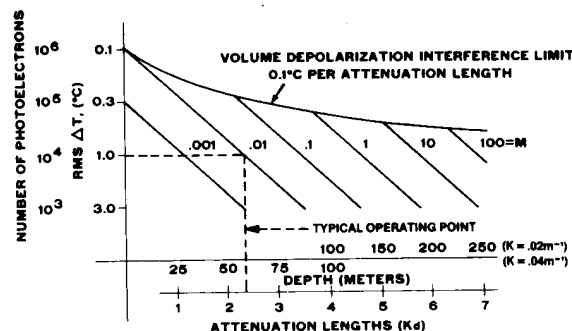


Fig. 2. Typical system operating map (100-m mixed layer).

particular water being measured and is highly variable among open ocean, continental shelf, and coastal waters. Table III, which is based on data published by Ferguson,³¹ lists the various types of ocean and coastal waters with values of diffuse attenuation coefficient, the range of the optimum transmission wavelength window, and the rate of laser beam power loss in dB per meter of depth penetration.

The performance of a Raman lidar subsurface temperature measurement system as a function of depth, water quality, and the other relevant operating parameters can be summarized by means of an operating map such as is shown in Fig. 2. The operating map of Fig. 2 has been calculated for a typical airborne open ocean measurement situation with a mixed layer depth of 100 m. The basic parameters on the map are the number of Raman photoelectrons collected as the ordinate with the depth as measured in attenuation lengths displayed on the abscissa. The derived quantities of temperature precision in °C and the depth in meters as a function of water quality are also shown as alternate ordinate and abscissa quantities, respectively. The operating lines on the map are drawn for various values of the parameter M , where M is defined as

Table III. Underwater Windows for Various Ocean Waters^a

Water type and location	Transmission window		
	K (m^{-1})	Loss (dB/m)	(nm)
Clearest ocean, open ocean; tropical and subtropical, below thermocline	0.02	0.087	430-470
Clearest ocean, open ocean; tropical and subtropical, above thermocline	0.03	0.130	440-480
Warm ocean, open ocean; tropical and subtropical, above thermocline	0.04	0.170	470-490
Cool ocean, open ocean; temperate subarctic and arctic, above thermocline	0.07	0.300	475-495
Shelf, continental shelf, surface to bottom	0.10	0.430	490-510
Coastal, coastal; relatively shallow water, surface to bottom	0.16	0.695	510-550
Very turbid, inshore coastal; harbor and bay water, surface to bottom	0.40	1.737	550-570

^a See Ref. 31.

$$M = \left(\frac{P_L}{20} \right) \left(\frac{\Delta R}{10} \right) \left(\frac{1}{R} \right)^2 T, \quad (2)$$

where P_L is the average laser power in watts, ΔR is the depth resolution in meters, R is the altitude of the aircraft in kilometers, and T is the integration time of the measurement in seconds. Thus, for example, for a system with $P_L = 0.2$ W, $\Delta R = 10$ m, $R = 1$ km, and $T = 1$ sec, the map parameter would be $M = 0.01$. This means that with such a system the allowed region of the operating map of Fig. 2 is to the left of the line labeled $M = 0.01$. A typical operating point is shown corresponding to a temperature accuracy of 1°C and a depth penetration of 60 m at the limit of a map function value of $M = 0.01$.

The map is constructed by using Eq. (1) to calculate the near surface (ordinate) values of the number of photoelectrons collected for each polarization for a given map parameter M . The over-all optical and photoelectric efficiency, the effective diameter of the collector, and the Raman scattering cross section are those given in Table II. The slope of the lines is determined by the transmission loss as a function of depth given by $\exp(-2Kd)$, where K is the diffuse attenuation coefficient, and d is the depth.

Also shown on the operating map is an upper boundary labeled volume depolarization interference limit. This represents the most significant interference to the measurement and is caused by depolarization due to transmission through natural waters. Analysis of data published by Duntley³² has shown that the depolarization effect will produce an uncertainty in a Raman spectral temperature measurement of the order of 0.1°C per attenuation length and in a Raman salinity measurement of the order of 1 part per 10^3 per attenuation length.

IV. Major Interferences and Noise Sources

An important aspect of the research effort has been to identify and quantify the major interferences and noise sources that laser Raman spectroscopic measurements of subsurface ocean temperature profiles would encounter. The purpose of this effort was to ensure that subsequent experiments would be properly designed and planned so that the significant questions concerning interferences and noise sources could be adequately answered.

The interferences and noise sources can be summarized as follows: surface wave effect as they influence both depth and lateral spatial resolution, and also as a depolarization noise source; volume transmission phenomena of differential attenuation and depolarization; and the non-Raman photon sources such as laser-induced fluorescence and ambient light backgrounds.

A. Surface Wave Effects

The effect of surface waves were found to relate in three significant ways to the subsurface measurement of temperature and salinity. These are (a) the differential transmission of orthogonal linear polarizations through the air-water interface, (b) the loss of depth resolution due to variable refraction angles produced

at a wavy water surface, and (c) the lateral error due to the same variable refraction angles.

The differential transmission of orthogonal linear polarizations through an oblique air-water interface in terms of typical wave spectra was investigated by means of exact 1-D calculations on an IBM 360 computer. New computer routines were written which used the basic Fresnel refraction equations.³³ Sinusoidal as well as finite amplitude trochoidal and Stokes waves³⁴ were employed in the program. The effect of variable crest height-to-wavelength ratios was investigated in order to study the effect of sea state on the measurement.

The results showed that even at the worst case sea state condition of a Stokes limit peak-to-peak wave amplitude-to-wavelength (H/L) ratio of 0.143, the effect is to introduce a bias of less than 1.0% in the Raman depolarization ratio measurement. This would mean less than a 1.0°C offset in the temperature measurement or a few parts per 10^3 error in the salinity measurement if uncorrected. It was concluded, therefore, that in the initial experimental configuration no attempt should be made to improve the accuracy by correlation on a pulse-to-pulse basis of the wave angle, an average over a given wave spectra being adequate for initial experimental investigation.

The quantitative nature of the effect is shown in Fig. 3, which is a plot of the differential polarization $\Delta B/B_\perp$ produced by oblique transmission through an air-water interface vs the incident angle θ_i . As shown, the effect is negligible for small angles and becomes nearly unity at angles approaching 90° . In a practical situation, the average differential polarization obtained by integration over typical wave spectra must be considered, and such integrated calculations were made using sinusoidal and finite amplitude trochoidal and Stokes waves of varying crest height-to-wavelength ratio.

Figure 4 shows the results of the calculations displayed as a plot of the effective differential polarization transmission $(\Delta B/B_\perp)_{\text{eff}}$ as a function of the peak-to-trough wave height-to-length ratio (H/L) for sinusoidal, trochoidal, and Stokes waves. The results show that for values of H/L less than the breaking wave Stokes limit of H/L equal to 0.143 the differential polarization is less than 6×10^{-3} . This means that the effect if un-

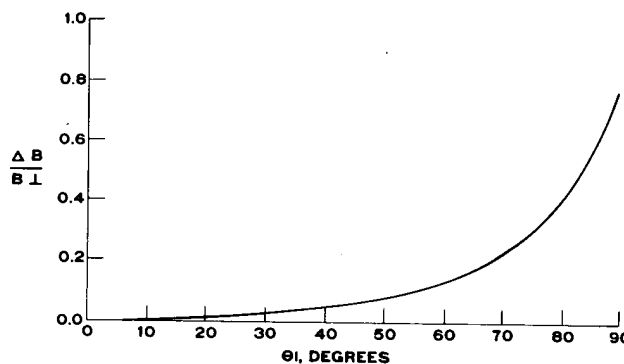


Fig. 3. Differential polarization vs incident angle.

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corrected will at worst produce an error bias in the Raman measurement of about 0.6°C in the temperature or 3–5 parts per 10^3 salinity concentration. The calculation also shows that the assumption of wave shape, i.e., sinusoidal, trochoidal, or Stokes, is not a significant factor in the integral of $\Delta B/B_{\perp}$ over the entire wave until the Stokes limit is greatly exceeded.

If the waves are small compared to the laser spot size on the water surface or if the measurement is made by time average of many laser shots randomly distributed on large waves, the above calculations are valid. For single pulse measurements with waves large compared to the laser spot size, the local slope of the wave should be monitored, and a correction made to the data. We have made calculations that show this to be possible.

The depth resolution depends on the laser pulse duration, the receiver bandwidth, and the properties of the water transmission medium, especially the refractive properties of the surface, i.e., the air–water interface. Off-the-shelf laser and receiver systems have demonstrated 10–20-cm depth resolution in bathymetric lidar systems,²⁶ which are generically similar to a laser Raman range gated temperature/salinity lidar system. Improvements in the direction of shorter laser pulse durations and improved receiver bandwidths and rise times are possible to incorporate into lidar systems. The major depth resolution limitation, at least for an airborne system, appears to be, however, the random refractive effects of the air–water interface at the sea surface.

A computer routine was written to describe the depth resolution as a function of sea state. Figure 4 presents plots of the results of the calculations of the fractional error in depth measurement vs H/L , the peak-to-trough wave height-to-length ratio. The calculations were made for three wave shapes: sinusoidal, trochoidal, and Stokes. It is apparent from the plots that the error in

depth measurement is not significantly influenced by the choice of wave model for values of H/L less than the Stokes limit of 0.143. The values plotted are the fractional error in depth measurement as averaged over a complete wave. Thus, it is seen that the fractional error in depth measurement is less than 0.3% for ocean waves having an H/L near the Stokes limits and nearer 0.1% for the more typical ocean waves with H/L from 0.06 to 0.08.

The refractive effects of the air–water interface at the sea surface will also influence the lateral resolution of the measurement volume that is attainable as a function of depth. The value of the lateral error is the product of the depth and $\sin(\Theta_i - \Theta_t)$, where Θ_i = inclination of laser beam to wave surface normal. The relative importance of this effect, when averaged over typical wave spectra, has been estimated using a computer program. A calculation using the fourth-order Stokes wave shape showed that at a depth of 100 m the lateral position of the measurement may be in error by as much as ± 10 m for waves near the limit of breaking. For less violent waves, having smaller values with a H/L ratio of 0.02 at a depth of 100 m the average lateral position error due to surface refractive effects would be 0.89 m.

B. Volume Transmission Phenomena

The effect of differential attenuation on the application of a two-color or band shape analysis of the liquid water Raman spectrum has been treated by previous investigators.⁸ The work reported here has extended the analysis to include in addition the effects of differential depolarization and the requirements for multi-wavelength polarization analysis for the Raman temperature and salinity measurement.

The data obtained by Duntley,³² which are shown in the graph of Fig. 5, clearly indicate that the decay of the degree of polarization of polarized beam of light as it passes through natural waters is an exponential function of the distance traversed. What is remarkable from the Duntley data is that over 80% of the original polarization remains even after traversing 20 attenuation lengths.

In a private conversation with Duntley he expressed the opinions that (a) to the extent investigated, all natural waters exhibit the same general exponential depolarization characteristics, (b) limited experimentation has been done on the depolarization of transmitted light in a variety of natural waters, (c) the fluctuations in the depolarization of transmitted light in natural waters is virtually a virgin territory for the experimentalist, and (d) the polarization information content of a beam of light is preserved essentially until the last photon has been absorbed, i.e., the attenuation coefficient is much larger, the order of 100 times larger, than the depolarization coefficient.

The scaling of the depolarization during transmission through natural waters and its effect on a Raman depolarization ratio temperature/salinity measurement has been estimated. Duntley's data, shown in Fig. 5, justify the assumption of the following exponential decay law:

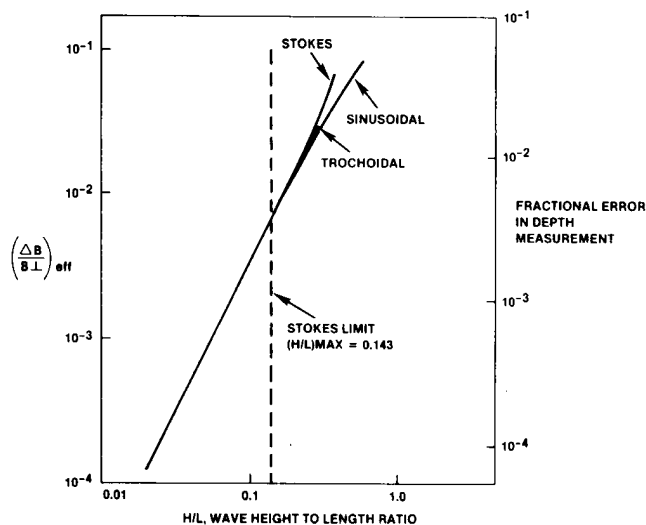


Fig. 4. Differential transmission of orthogonal linear polarizations and fractional error in depth measurement due to refraction as function of H/L for Stokes, trochoidal, and sinusoidal waves.

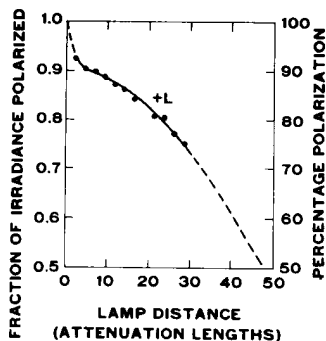


Fig. 5. Depolarization during transmission through natural waters obtained by Duntley.³²

$$(dI_p)/(dx) = \rho_s I_p, \quad (3)$$

where I_p is the polarized portion of a beam of light, s is the water transmission distance, and ρ_s is the depolarization coefficient.

An average value of 0.01 was taken as an empirical proportionality constant between the diffuse attenuation coefficient K and the depolarization coefficient ρ_s , this being an average of the two known literature values^{32,35} of the constant.

Results of calculations show that if the depolarization effect were neglected and left uncorrected, a temperature error ΔT of about 1.6°C per diffuse attenuation length and a salinity error ΔS of about 7 parts per 10³ per diffuse attenuation length could occur. The results also show that if the proportionality between ρ_s and K is known to within 10%, corrections can be made which result in a residual uncertainty of 0.1°C in temperature and 0.7 parts per 10³ in salinity for each diffuse attenuation length traversed.

This analysis indicates that based upon (a) the lack of experimental work published or known on the variability of the depolarization of transmitted light in natural waters and (b) the sensitivity of the temperature and salinity measurement to the ρ_s depolarization coefficient, a major thrust of further research should be to study the extent of the variability of the proportionality between ρ_s and K and thus better define the residual temperature and salinity bias that can be expected.

The impact on experiment designs and test plans is that a software capability to determine K through differential analysis of the Raman signal as a function of depth should be included. Independent experimental measurement of the proportionality constant between ρ_s and K should also be investigated for a variety of natural waters.

C. Differential Depolarization—Theoretical

Because of the importance of the differential depolarization effect described above, some effort has been devoted to calculations that attempt to describe from basic Mie scatter calculations the depolarization in the forward direction in natural waters. The motivation

was both to explain the previous experimental results of relatively weak, i.e., $\rho_s \approx 0.01K$, depolarization in the forward direction and also to guide future efforts in the directions of relevant further calculations and/or experiments.

The depolarization of the forward-scattered component of an underwater light beam was investigated. This forward-scattered component dominated the direct attenuation beam after a few scattering lengths and is, therefore, the significant component for remote probing of subsurface ocean temperatures. Computations, using the Mie formalism, were made of the depolarization within a 5° cone of light, single-scattered by spherical particles which approximate in sizes and refractive indices reported for ocean water in the literature.³⁶ Essentially no depolarization ($\ll 1\%$) was calculated for single scattering. This result is in accord with previous observations indicating (a) negligible depolarization of the forward-scattered beam of a laser after eighteen scattering lengths of lake water³⁷ and (b) 20% depolarization of light after traveling 20 scattering lengths of lake water.³² Such polarization as occurs in natural waters may be the result of scattering from small particles, nonspherical particles, and/or many scattering events. In either case direct measurements of depolarization in various types of seawater would probably be more useful than complex and idealized calculations. In summary, the experimental observations of weak depolarization in the forward beam are to be expected from the character of the Mie single scatter process for the large particles which dominate seawater scatter.

D. Differential Attenuation and the Need for Multiwavelength Polarization Detection

The effect of the differential attenuation of light through natural waters and its impact on the Raman depolarization detection technique have also been investigated as part of the effort of planning an experimental apparatus design. The main conclusion was that a simultaneous multiwavelength detection or wavelength-scanning detection capability is required if a reasonable depth capability is to be obtained, even using the polarization ratio technique. Previous studies³⁵ had suggested that although differential attenuation was a problem for two-color measurements, it would not affect a polarization ratio scheme.

The physical basis for this conclusion is the following. The Raman circular depolarization coefficient for liquid water varies across the band from values of 0.2–0.8. If the entire Raman band is detected with a single detector, an average ρ_R will result. The average ρ_R is effectively

$$\rho_R = \frac{\int I(\lambda) \rho_R(\lambda) d\lambda}{\int I(\lambda) d\lambda}, \quad (4)$$

where the $\rho_R(\lambda)$ is weighted by the intensity $I(\lambda)$.

Differential attenuation as, for example, would be caused by traversing several attenuation lengths of water would cause a distortion of the Raman band shape, i.e., the $I(\lambda)$ factor, and thus introduce an error in the effective $\bar{\rho}_R$ measured. A solution is to use multiple band segments of a bandwidth such that the per-

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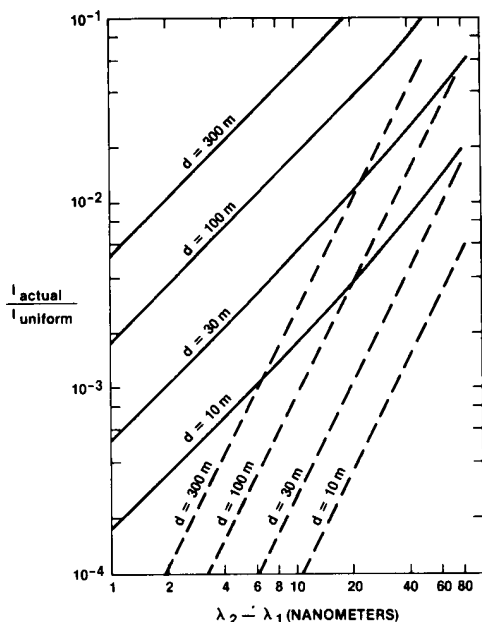


Fig. 6. Differential attenuation vs wavelength separation-with depth as a parameter at the minimum of the diffuse attenuation coefficient (dashed lines) and 10 nm from the minimum (solid lines).

percentage distortion is acceptable in each band segment. The polarization ratios are thus obtained on a band segment by band segment basis and then combined with suitable weighting functions to yield the temperature and salinity information.

The relationship among the bandwidth of the individual Raman band segments, the accuracy required, and the differential attenuation was addressed. The practical result was that a required spectrometer resolving power could be specified for the experimental apparatus design.

Calculations were carried out using the diffuse attenuation coefficients (K) published by Ferguson³¹ for natural ocean water, which can be fit by parabolic functions of wavelength such as $K = \beta(\lambda_1 - \lambda_0)^2 + \gamma$, where β and γ are constants which are functions of water quality and type. Using a typical value of $4 \times 10^{-6} \text{ m}^{-1} \text{ nm}^{-2}$, results were obtained showing the residual error remaining as the Raman band was piecewise detected by means of multiwavelength analysis.

Based on this analysis, the fractional change in signal between two wavelengths λ_1 and λ_2 caused by differential transmission compared to a uniformly transparent medium is given by the following equations:

$$\frac{I_{\text{actual}}}{I_{\text{uniform}}} = 1 - \frac{\exp[-2d\{\beta(\lambda_2 - \lambda_0)^2 + \gamma\}]}{\exp[-2d\{\beta(\lambda_1 - \lambda_0)^2 + \gamma\}]} \quad (5)$$

$$\frac{I_{\text{actual}}}{I_{\text{uniform}}} = 1 - \exp[-2d\beta[(\lambda_2 - \lambda_0)^2 - (\lambda_1 - \lambda_0)^2]] \quad (6)$$

The plots in Fig. 6 are based on the above equations and show the signal error introduced as a function of the bandwidth with depth as a parameter. The dashed lines are for $\lambda_1 - \lambda_0 = 0$, meaning symmetric alignment of the Raman band with the minimum of the diffuse

attenuation (K) curve, and the solid lines for $\lambda_1 - \lambda_0 = 10 \text{ nm}$, i.e., 10-nm displacement of the Raman band from the minimum of the K curves.

Based on these calculations it is clear that an experimental wavelength-scanning capability with a wavelength resolution the order of a few tens of nanometers is necessary. It is also obvious from these calculations that there is a requirement for a tunable laser to position the Raman water band at or near the minimum of the diffuse attenuation (K) vs wavelength curve.

E. Non-Raman Photon Sources of Noise

Laser-induced fluorescence backgrounds as well as ambient light backgrounds are common sources of interference in remote Raman measurement systems. Such effects can be reduced by using the following standard techniques.

The detection system should be limited to only those wavelengths that are within the Raman band, and synchronous time gating techniques should be employed. The use of background subtraction by sampling the ambient background during the laser interpulse period should also be included in the experiment. In addition, subtraction of laser-induced fluorescence can be accomplished by measurement of the laser-induced spectral background level at wavelengths adjacent to the Raman water band.

The following discusses the salient features of ambient light and laser-induced fluorescence-like phenomena when viewed as non-Raman photon noise sources.

Standard references³⁸ on remote laser Raman applications show that the limiting SNR that can be achieved in a remote Raman system is the shot noise in the laser Raman signal itself. Such a Raman system is assumed in the planned experiments.

The contribution of ambient background illumination to the SNR can be shown³⁰ to increase the time required to make a Raman measurement with a fixed SNR as follows:

$$T = \left(\frac{S}{N}\right)^2 \frac{1}{P_{\text{avg}}} \left(1 + \frac{2P_{\text{NEP}}}{P_{\text{pk}}}\right) \quad (7)$$

where T is the time required to make a measurement, S/N is the SNR, P_{avg} is the average laser power, P_{pk} is the peak laser power, and P_{NEP} is the noise equivalent power of the ambient background illumination. Thus, the important parameter is the ratio of the background illumination or the noise equivalent power to the laser peak power.

The upward irradiance of sunlight near the sea surface is given by Jerlov³⁹ as being $7 \text{ mW/cm}^2\text{-}\mu\text{m}$ at a wavelength of 500 nm. Using this number of irradiance and neglecting the effects of sun glints and specular reflection, a P_{NEP} -to- P_{pk} ratio of slightly greater than unity was computed for an airborne platform using the Raman system parameters previously assumed in the performance estimate calculations. This means that a measurement time of about three times longer will be required during the daylight hours to obtain the same SNR that could otherwise be obtained at night.

In a boatborne experiment, because the Raman signal

level using the same laser source will be considerably higher, the P_{NEP}/P_{pk} ratio is expected to be small compared with unity. However, because better than 1% measurements are desired, a capability should be designed into experiments to sample the background ambient light level in the time interval between laser pulses. This background measurement should independently sample each of the two polarization channels so that background subtraction may be applied independently to each polarization signal before a polarization ratio is computed. This is important because the upward irradiance from the sea is known to be partially polarized.

The presence of laser-induced fluorescence-like background noise has been shown³⁰ to add another term to the equation which expresses the time required to make a Raman measurement with a fixed SNR as follows:

$$T = \left(\frac{S}{N}\right)^2 \left(\frac{1}{P_{avg}} 2F + 1 + \frac{2P_{NEP}}{P_{pk}} \right), \quad (8)$$

where the additional term F is defined as the ratio of the laser-induced fluorescence signal to the Raman signal.

It should be noted that preliminary field experiments conducted in natural coastal and ocean waters by CGC personnel and described in the following sections showed a fluorescence-to-Raman ratio as low as 0.01 or less when using a 337-nm laser source. Such data should be extended to cover the entire visible spectrum by using a tunable laser source, and such spectral coverage should be obtained from a variety of coastal water types.

V. Experimental Results

A. Description of Raman Lidar Equipment

The subsurface water Raman spectra were obtained using a Raman lidar system originally designed and used by Leonard and Caputo²² as a single-ended transmissometer for airport glide slope visual range applications. This equipment was recently modified by CGC to include a capability to measure atmospheric profiles of water vapor and temperature in addition to atmospheric transmission profiles. As such, the system was nonoptimal for subsurface water measurements, but enabled useful new information to be obtained.

A block diagram of the equipment is shown in Fig. 7. The laser source is a pulsed nitrogen laser operating at 337.1 nm and producing pulses of 100-kW peak power with an effective pulse duration of 10 nsec at a pulse repetition rate of 500 Hz. The nitrogen laser uses an unstable resonator cavity and produces a beam symmetric in the far field with a divergence of approximately 2 mrad. The output from the laser is passed through an interference filter which passes the 337.1-nm laser line with a high efficiency, but blocks spontaneous emission occurring in the laser gas discharge in the O—H Raman spectral region near 380.0 nm.

The photons collected by the receiver optics are passed through a liquid filter and into a double 0.25-m

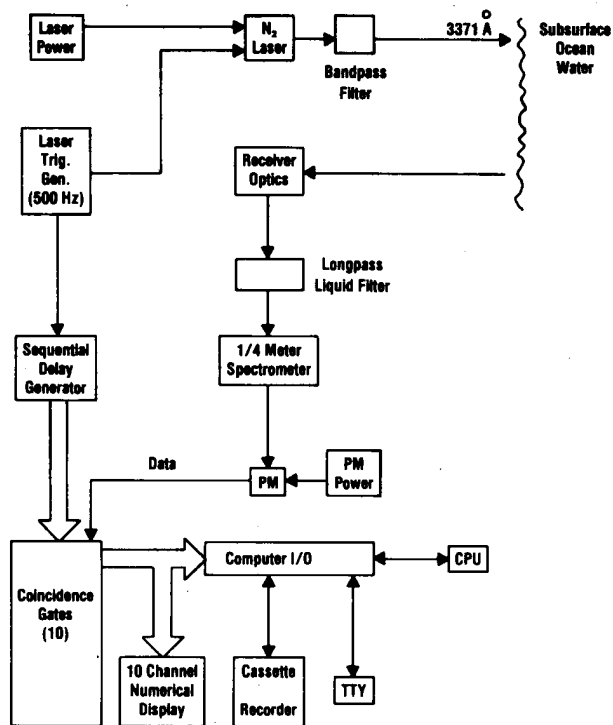


Fig. 7. Block diagram of Raman lidar equipment.

focal length scanning spectrometer having a 0.5-nm spectral resolution. The wavelength scanning of the spectrometer produces a spectral scan of the liquid water Raman O—H stretching band with sufficient resolution so that the monomer and polymer components can be resolved and a water temperature determined.

The liquid filter, a water solution of 2,7-dimethyl-3,6-diazacyclohepta-1,6-dieneperchlorate in a quartz walled cell, has the property of essentially complete isotropic volume bulk absorption of 337.1 nm, but with nearly complete transparency at wavelengths of 350 nm and longer. This filter is used for blocking the strong on-frequency return at 337.1 nm, which is reflected from the water surface and which the spectrometer alone is not able to reject adequately. It is far superior in this regard than the best interference filters commercially available, both in transmission characteristics and in angle requirements.

The Raman photon output from the spectrometer is detected by a RCA 8850 photomultiplier. The Raman photoelectron signal and a gate pulse suitably synchronized and delayed with respect to the laser firing are combined in ten separate coincidence gates, the output from which are recorded using direct memory access (DMA) techniques with a Data General NOVA 1220 computer. The number of pulses occurring during the same data taking interval is also recorded. The ratio of the Raman photoelectrons to laser pulses recorded over a given time interval is the basic data obtained. The ten coincidence gates provide Raman data at ten separate range locations which can be varied both

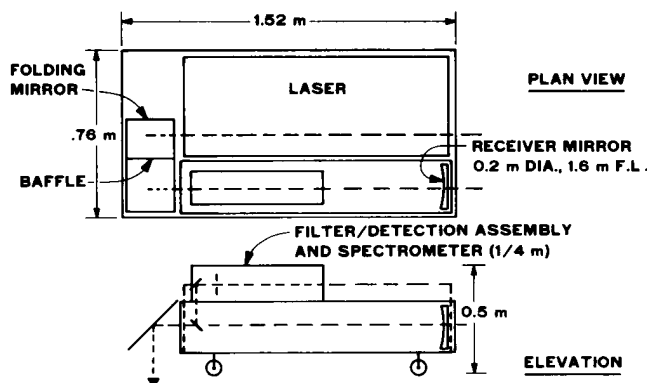


Fig. 8. Plan view and elevation of USNS *Hayes* Raman lidar equipment.

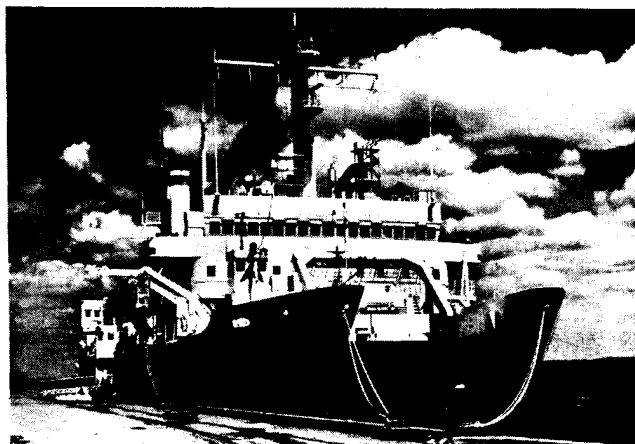


Fig. 9. USNS *Hayes*.

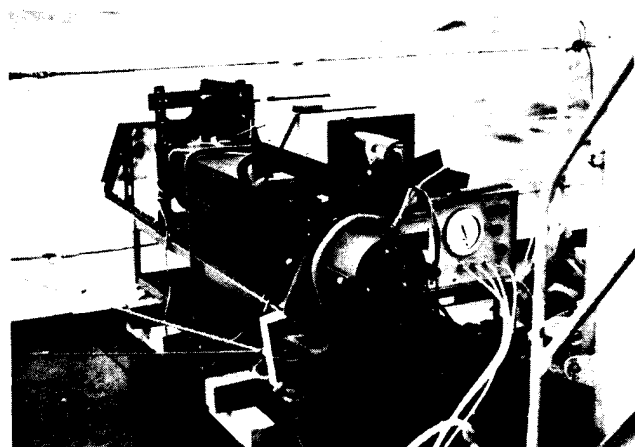


Fig. 10. Raman lidar transceiver in place on *Hayes* afterdeck.

in width and spacing over the 30–330-nsec and 50–550-nsec ranges, respectively.

The data taking is fully automated. The computer can be directed through the teletype (TTY) to specify the number of laser pulses over which to record data at each wavelength and the maximum and minimum wavelengths and the wavelength increments of each spectral scan. The data obtained are printed on the TTY in tabular form and also recorded on cassettes. A 10-channel numerical display of the data is also provided.

The plan and elevation views of the Raman lidar transceiver equipment are shown in Fig. 8. The equipment is secured to a wheeled cart which was used on the afterdeck of the research vessel *Hayes*. The 45° mirror was rotated 180° to convert the system from an upward looking atmospheric lidar to a downward looking subsurface oceanographic lidar.

Figure 9 is a photograph of the USNS *Hayes*, which illustrates the unique twin hull character of the research vessel. Figure 10 shows the Raman lidar transceiver in place on the afterdeck of the *Hayes* in a typical data taking mode positioned to view the ocean water in the wake between the hulls. Subsurface Raman water spectra were obtained both with the ship stopped and as a function of speed while under way. The effects of foam and air bubbles in the wake were observed to cause increased signal attenuation as the ship speed increased, but no measurable distortion of the Raman spectrum. The difference in Raman signal amplitude between a dead stop and full speed was about an order of magnitude.

B. Experimental Field Measurements—*Hayes* Cruise

In this section the field measurements and the data obtained to date are described. The first preliminary field experiments were conducted aboard the Computer Genetics Corporation research vessel, the *Makai*, and Raman spectra were obtained from various depths in the Annisquam River, a tidal estuary in Massachusetts. The data were analyzed, and a spectral temperature was obtained which agreed with laboratory calibrations. This work has been reported elsewhere.²⁹

More recently (May–June 1977), resolvable Raman subsurface water temperature spectra were obtained in five open ocean locations from the decks of the Naval Research Vessel, USNS *Hayes*, during a North Atlantic/Mediterranean research cruise. The locations shown in Table IV ranged from the colder North Atlantic waters (sea surface temperature 4.7°C, 15 May), 100 miles (160 km) southeast of Cape Race, Newfoundland, to the warmer Mediterranean Sea (19.7°C, 2 June), 160 km west of Sicily. Raman spectra were documented and recorded from depth regions of 0–10 m, 10–20 m, and 20–30 m.

The significant new information and conclusions derived from these *Hayes* experiments are the following: (1) the Raman spectra of the open ocean waters that were investigated for the first time were found to be essentially free of 337-nm laser-induced interferences, (2) Raman spectral temperature measurements

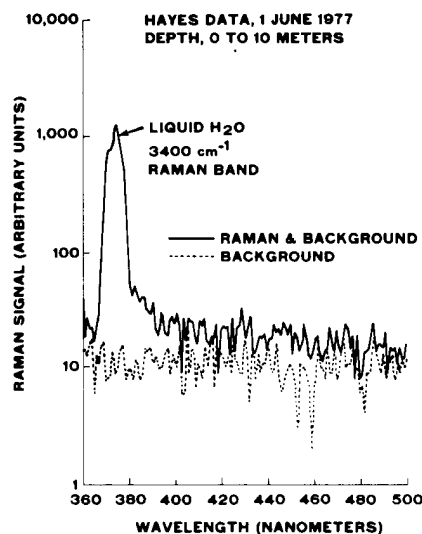


Fig. 11. Raman water band plus laser-induced background.

to a relative accuracy of $\pm 1^\circ\text{C}$ were made in natural ocean water from an ocean research vessel while under way, (3) Raman spectral measurements of the subsurface temperature gradient to a depth of 30 m were obtained, and (4) the experimental results strongly support the previous concepts and system design calculations for the exploitation of induced Raman spectra for the remote sensing and quantitative measurement of subsurface ocean temperature.

C. Data Analysis

Several different experiments were performed and data obtained as follows:

1. Broad Spectral Scans

The purpose of the broad scans was to study the total 337.1-nm induced spectrum (i.e., fluorescence) in addition to the water Raman band itself. The fluorescence-to-Raman ratio is important for Raman system signal-to-noise considerations, and measurements of this ratio in natural water are necessary for predicting system performance.

The spectra plotted on a logarithmic scale in Fig. 11 show typical raw laser-induced data obtained at wavelengths between 360 nm and 500 nm. The background signal obtained with the laser blocked is also shown for comparison. The conclusion to be drawn is that the 3400-cm^{-1} liquid water Raman band is by far the most prominent feature of the spectrum and that the laser-induced fluorescence is much less than a 1% effect. The response of the Spex 0.25-m spectrometer to a delta function wavelength impulse has not yet been calibrated, and some significant portion of the residual induced signal may be an instrumental effect.

The data shown in Fig. 11 were obtained in the Mediterranean 100 miles south of Mallorca at

$37^\circ 50.5'\text{N}$, $03^\circ 47.1'\text{E}$ on 1 June 1977. The character of the data with respect to fluorescence interference at the other Mediterranean location near Sicily and in the Atlantic locations southeast of Cape Race, Newfoundland, and northwest of the Azores was basically the same.

2. Raman Band Shape Analysis for Temperature

The laser Raman spectra of the ocean waters clearly show temperature-dependent effects. The spectra of Fig. 12 compare Labrador Current water with Gulf Stream water. The ground truth measurements of temperature were 4.7°C and 15.7°C as shown. Both spectra were for water in the first 10 m of depth. Analysis of the two band shapes with the standard two-color technique shows that the polymer component decreased by 13% between the Labrador Current and Gulf Stream with a spectral temperature difference of 13°C compared with the measured difference of 11°C .

3. Raman Spectra as a Function of Depth

Figure 13 shows raw Raman data obtained simultaneously at the three depths of 10 m, 20 m, and 30 m at the Mediterranean location west of Sicily. The characteristic Raman band shape is clearly observable at all three depths. The effect of differential attenuation with the 337-nm laser wavelength causes an apparent increase in spectral temperature as the depth increases, whereas simultaneous XBT records show that the temperature was essentially constant in this range of depth. Analysis using Gaussian deconvolution techniques (see Appendix) shows that a differential diffuse attenuation coefficient $dK/d\lambda$ of 0.003 m^{-1} per nm would account for the effect and can be used to derive

Table IV. Subsurface Raman Experiments at Sea

Location	Date	Sub-surface temperature
100 miles SE of Cape Race, Newfoundland 45°54'N, 51°03'W	19 May 1977	4.7°C
300 miles NW of Azores 43°54'N, 34°29'W	22 May 1977	15.7°C
100 miles S of Mallorca 37°59'N, 03°47'E	1 June 1977	19.2°C
100 miles W of Sicily 38°05'N, 10°33'E	2 June 1977	19.8°C

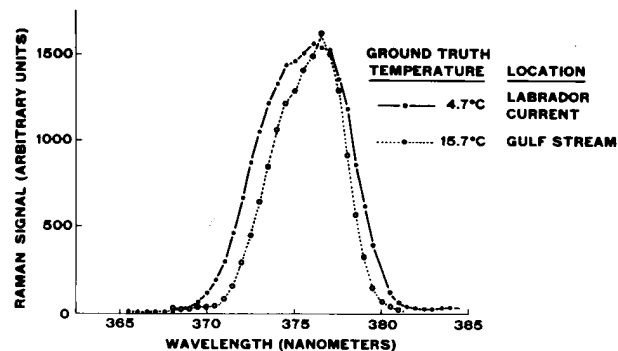


Fig. 12. Raman spectra of Labrador Current and Gulf Stream.

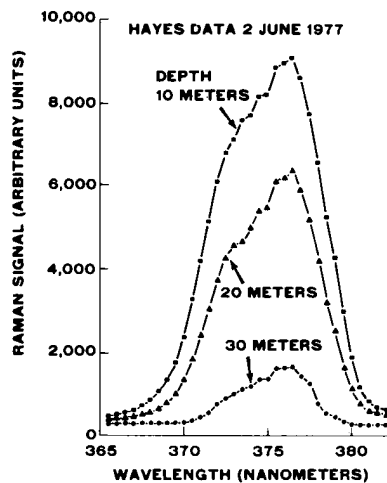


Fig. 13. Simultaneous Raman spectra at depths of 10 m, 20 m, and 30 m.

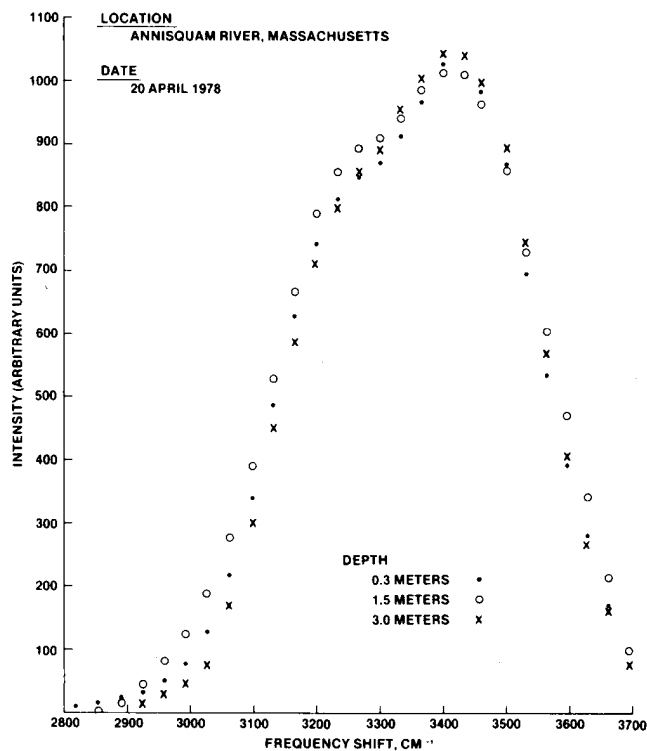


Fig. 14. Raman spectra from three depths in Annisquam River.

Table V. Summary of Coastal Temperature Measurements

Depth (m)	Integral ratio	Raman temperature (°C)	Ground truth temperature (°C)
0.3	2.08	8.1	6.7
1.5	2.01	4.6	6.1
3.0	2.03	5.7	5.6

the correct temperature as a function of depth from the data. This value of differential attenuation is consistent with published data¹¹ for ocean-type water at the uv wavelength used, although no independent ground truth measurements of the diffuse attenuation coefficient were available at the time the experiments were performed.

It should be noted that the use of a blue-green laser in the 450–500-nm wavelength region will enable penetration in the open ocean to about 100 m with similar Raman spectral resolution as that already obtained at a depth of 30 m. The reason is that, based on published data,²³ the diffuse attenuation coefficient is expected to be a factor of 3 smaller in the blue-green than at the 337-nm UV wavelength used in the experiments. It should also be noted that significant improvements in temperature measurement capability as a function of depth are expected with the use of polarization sensitive detection and that field experiments in open ocean waters using such techniques with blue-green tunable lasers are now being planned.

D. Experimental Field Measurements—Coastal Results

A dye laser operating at 470 nm was added to the pulsed nitrogen laser lidar system and utilized in experiments conducted in Massachusetts coastal waters in November 1977 and in March and April 1978 using the CGC research vessel *Makai*.

The new results demonstrate that Raman temperature profiles are attainable in coastal waters, at least in the first optical attenuation length, using a simple two-color analysis procedure. As an example of such results, Fig. 14 shows Raman spectra obtained at three depths in the Annisquam River between Babson Point and Wheeler Point on 20 April 1978. These Raman spectra were obtained at depths of 0.3 m, 1.5 m, and 3.0 m together with simultaneous thermocouple ground truth readings at the same depths. The spectra plotted in Fig. 14 were normalized to have the same average peak value so that the relative shapes of the bands from the different depths could be analyzed to obtain temperature as a function of depth.

The two-color temperature analysis was carried out by taking for each band the ratio of the integral of the Raman signal in the 3100–3400-cm⁻¹ wavenumber region to the integral in the 3400–3700-cm⁻¹ wavenumber region. Previous calibrations have shown that this integral ratio is temperature sensitive with a negative differential sensitivity of about 1% per °C. The results

are shown in Table V which displays the Raman temperature profile and the ground truth temperatures as a function of depth. The rms temperature difference between the two sets of data is $\pm 1.2^\circ\text{C}$.

A diffuse attenuation coefficient (K) of 0.3 m⁻¹ was obtained from the same data by analysis of the exponential decrease in the amplitude of the Raman signal as a function of depth, taking also into account the decrease in effective solid angle of the receiver as the depth increases. The value of K obtained is consistent with Jerlov's value for medium quality coastal water in the wavelength region near 500 nm. There is, thus, also reasonable validity to the assumption that the Raman data from the first 3 m of depth fall within the first diffuse optical attenuation length. In future field work we plan to have diffuse attenuation ground truth in addition to temperature ground truth.

This work was supported in part by NASA Wallops Flight Center and the Office of Naval Research.

Appendix: Deconvolution of Raman Band Using Symmetric Gaussians

A mathematical deconvolution procedure has been developed to analyze the Raman water band spectra using a least-squares fit of symmetric Gaussian functions. This procedure was an attempt to maximize the SNR of the temperature measurement by essentially using all the data in the band to determine a spectral temperature rather than merely using a two-color ratio.

The choice of Gaussian components for the deconvolution does not appear to be supported by a theory of Raman line shapes; however, Walrafen⁵ in his early work with the water Raman band and more recently Dylis⁴⁰ have found Gaussian line shapes to be empirically satisfactory. We have used in our analysis the four Gaussian components that were employed by Walrafen whose frequencies and halfwidths are as follows: (1) 3225 cm⁻¹, 225 cm⁻¹; (2) 3425 cm⁻¹, 175 cm⁻¹; (3) 3520 cm⁻¹, 150 cm⁻¹; (4) 3612 cm⁻¹, 150 cm⁻¹. In addition a fifth Gaussian component reported by Dylis at 3060 cm⁻¹ was used with a halfwidth of 225 cm⁻¹.

A computer program was written to process the experimental Raman data which performs the following basic operation:

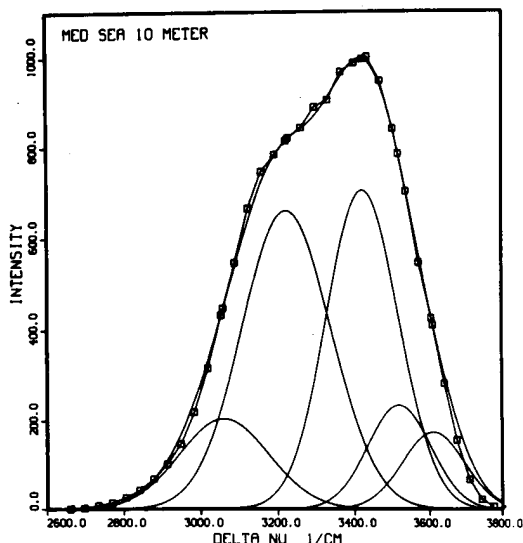


Fig. 15. Deconvolution of water Raman spectrum into symmetric Gaussian functions.

(a) The raw data were averaged over a prespecified number of spectral scans. This type of coherent addition of spectra was useful in filtering low-frequency noise such as the effect of the wake of the boat.

(b) Measurements of the laser-induced signal at wavelengths both longer and shorter than the Raman band were used to estimate the background level which was subtracted.

(c) The data were multiplied by an exponential factor to correct for differential attenuation as follows: $\exp[(dK/d\lambda)(h)(\lambda_0 - \lambda)]$, where $dK/d\lambda$ is the wavelength slope of the diffuse attenuation coefficient, m^{-1} per nm, h is the water depth in meters, and λ_0 is the median wavelength of the band.

(d) A three-point smoothing function was applied to the data.

(e) An iterative least-squares procedure was employed to select the best fit to data of the five symmetric Gaussians of preselected frequency and halfwidth.

As an example of this procedure, the deconvoluted data of 2 June 1977 obtained at a depth of 10 m in the Mediterranean are shown in the computer generated plot of Fig. 15. The squares connected by straight lines represent the Raman data. The solid curve is the sum of the Gaussian components obtained by the least-squares fit.

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