

# Lidar Field Experiments for Monitoring Sea Water Column Temperature

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## ABSTRACT

Up to now water column temperature can be remotely detected only by the LIDAR technique. This is performed by the analysis of Raman OH stretch spectrum, which is affected by temperature.

In this work remote water Raman spectra, obtained during an oceanographic campaign, are presented and discussed. These data are a first approach to high resolution in LIDAR Raman spectroscopy, showing good perspectives for this LIDAR technique.

## INTRODUCTION

Water column temperature is a fundamental parameter for the study of the marine environment. It provides useful information for the knowledge of biological processes, sea-water properties and climatic features complementing the data relative to the sea surface temperature, routinely determined by passive sensors. It can be also useful for the localisation of fresh-water submarine springs or industrial discharges.

At present LIDAR remote sensing is the only technique capable of measuring depth resolved water temperature profile without a direct interaction with the sample. From this point of view, remote sensing can offer many advantages in comparison with the traditional methods for sea-water column temperature measurements. Actually, the latter require a long time since are based on a direct measurement into the water column. Moreover, the application to wide areas produces prohibitive costs. On the contrary, a LIDAR system could measure water column temperature providing a map also with depth resolution in a short time.

Water temperature determination by a LIDAR system is performed by the analysis of the water Raman spectrum in

the OH stretch region ( $3400\text{ cm}^{-1}$ ). Since the bonds involved in the Raman scattering are modified by temperature variation, the spectrum is temperature-dependent (Walrafen *et alii*, 1986; Angell and Rodgers, 1984). Even if a precise physical interpretation of this temperature dependence is still under investigation, this effect can be exploited for this LIDAR application. In addition, this Raman signal is intense in remote-sensing measurements since a large number of molecules are excited along the water column.

Laboratory experiments investigated the feasibility of this method to water temperature measurement (Schwiesow, 1971; Chang *et alii*, 1974) and up to now only few field measurements have been performed (Leonard *et alii*, 1977; Leonard *et alii*, 1979).

## 1. LABORATORY EXPERIMENTS

Laboratory experiments were carried out to investigate those temperature-sensitive parameters suitable for remote-sensing measurements. It is essential to consider the work conditions imposed by in-field operation: for this reason relative measurements, such as intensity ratios or relative shifts, have been considered more suitable than absolute measurements. The latter are not considered in this work, although their temperature dependence might be interesting.

Laboratory experiments were performed on both a pure liquid water sample and a synthetic seawater one. The set of data obtained on the pure water sample and the relative results are presented and discussed in a previous work (Breschi *et alii*, 1992). The sample of synthetic sea water is made up by a standard solution of salts in distilled water, usually employed to reproduce sea water for laboratory seaweed cultures and for other marine biological experiments. The salinity is 33 ppt.

### 1.1 Experimental setup

The experimental setup is shown in Figure 1: the beam of an Argon ion laser (Spectra Physics, Model 165), tuned on the 514.5 nm line with 0.5 W at the output, was focused on the water sample kept at a constant temperature with a suitable temperature controller. The sample temperature was varied from 2°C to 40°C. This range widely covers the water temperatures which can be found in the sea at mid-latitudes. The water sample was kept inside a carefully cleaned spectrophotometer cuvette: the last one is inserted in a metal cuvetteholder with hollow walls, allowing a liquid flow from the temperature control system. Free spaces in the

cuvette walls allow the excitation and the detection of the water Raman signal.

The temperature was directly measured setting a thermocouple into the cuvette as close as possible to the region in which the laser beam was focused and the signal collected. The temperature was registered with an accuracy of 0.1°C. The Raman signal was collected at 90° by a focusing system coupled to the entrance slit of a 60 cm focal-length triple-monochromator (TRIPLEMATE 1877, SPEX). The stray-light level of the monochromator was  $10^{14}$  at 10 bandpass units from the laser line. Finally, the signal was detected by an Optical Multichannel Analyser (EG&G Model 1463 with a 1421B-512-HQ detector).

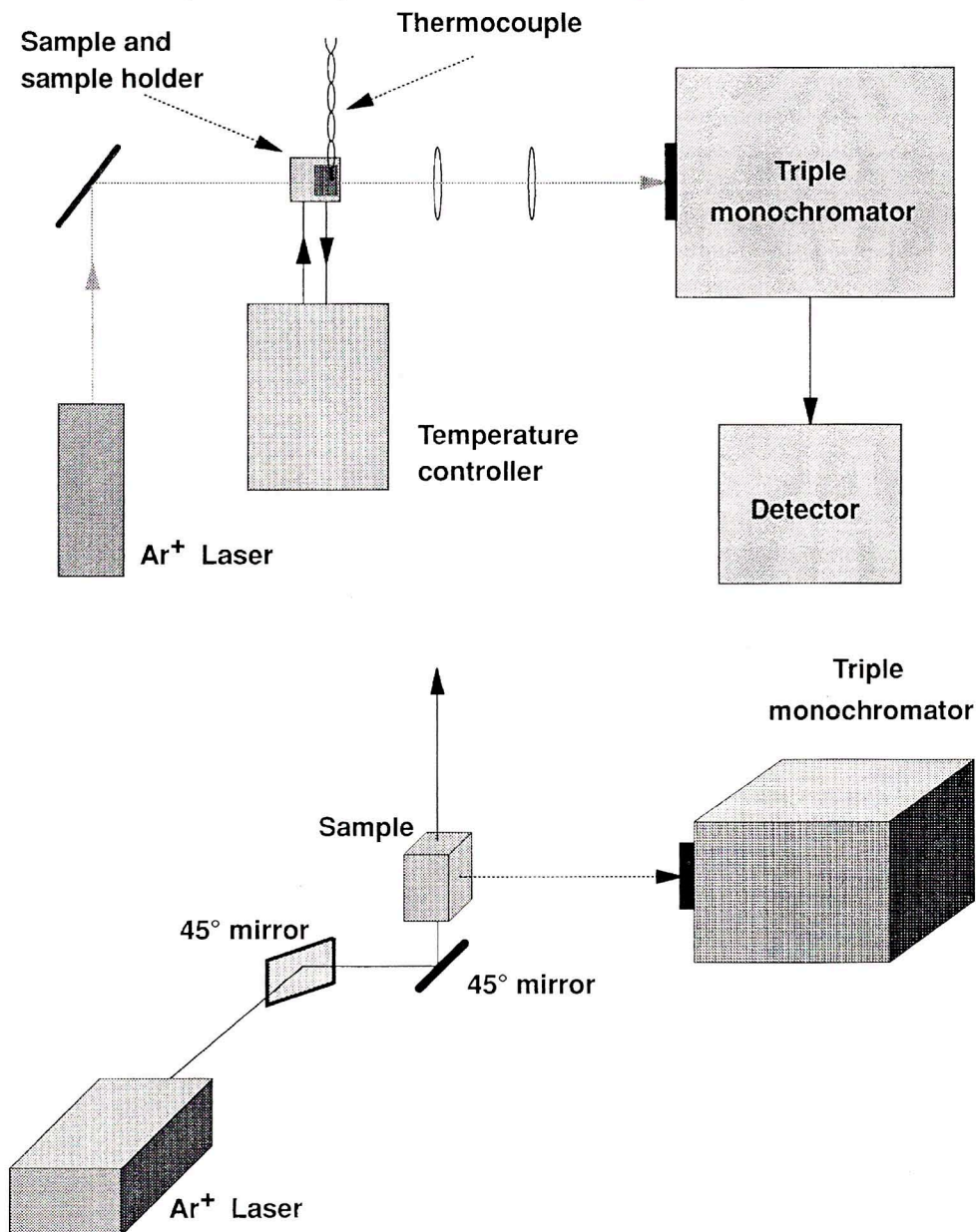


Fig. 1 - Laboratory measurements on a synthetic sea-water sample: (a) Block diagram of the experimental set-up. The excitation laser beam is upwarding with respect to the figure plane by a 45° mirror placed below the sample cuvette. (b) Sketch of the laser path and of the detected Raman signal.

## 1.2 Results and discussion

Laboratory Raman spectra are presented in Figure 2: the spectra are normalised to the area around the isosbestic point. All the spectra show approximately two bands whose intensities change with temperature: increasing temperature, the intensity of the low-frequency part of the spectrum decreases, while the other one increases. The same behaviour was observed for the pure water sample (Breschi *et alii*, 1992).

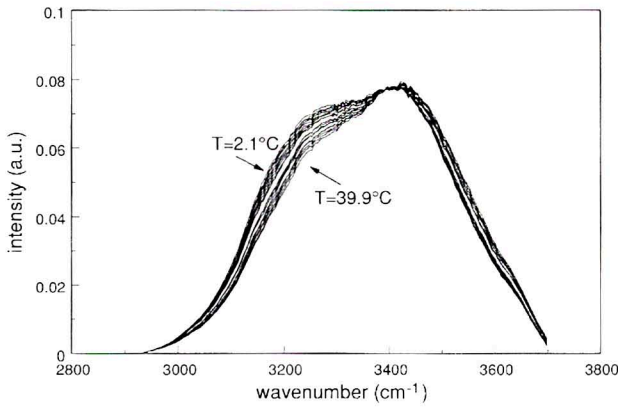


Fig. 2 - Laboratory Raman spectra on synthetic seawater sample. The spectra were normalized to the area around the isosbestic point.

The spectra were analysed with gaussian components using a nonlinear least squares method. Two Raman spectra at different temperatures and their fits with two gaussian components are shown in Figure 3. Although fits with more components are slightly more accurate (Walrafen, 1967; Breschi *et alii*, 1992), the two more intense components already give a reasonable sensitivity to temperature. So, it

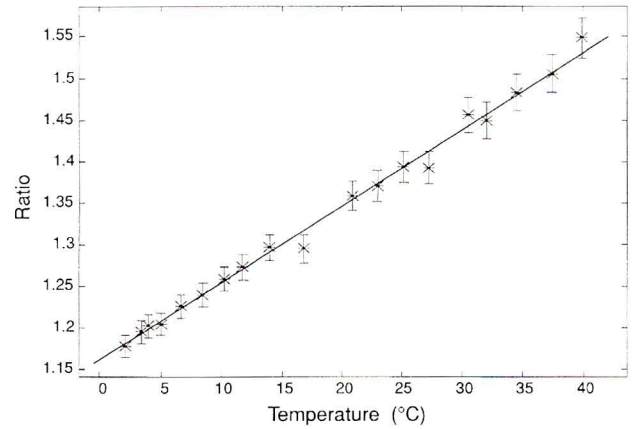
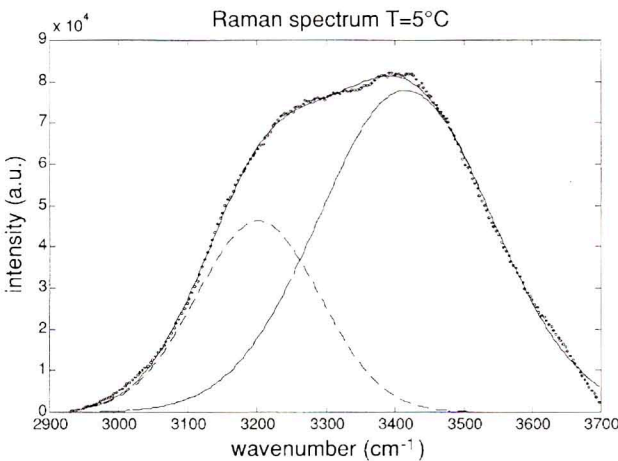


Fig. 4 - Gaussian normalised intensities ratio as a function of sample temperature.

has been used a two-gaussian fit, which also simplifies the data elaboration procedure especially in view of real-time results during field operation.

The ratio between the intensities of the two gaussians, normalised to their widths, is reported vs. temperature in Figure 4: the data were fitted with a  $y = ax + b$  line whose coefficients, obtained with the least squares method, correspond to the values of  $a = 0.0092 \pm 0.0003^\circ\text{C}^{-1}$  and  $b = 1.161 \pm 0.006$ . The  $a$  coefficient determines the sensitivity of the method and its value gives a variation of about 9% in the ratio when temperature varies by  $10^\circ\text{C}$ . This sensitivity value agrees with that observed by others with the “two-colours technique” (see e.g., Leonard *et alii*, 1979) instead of a gaussian fitting.

The intensities ratio is a parameter that varies linearly with temperature and is free from absolute measurements, so it is suitable for remote-sensing applications.

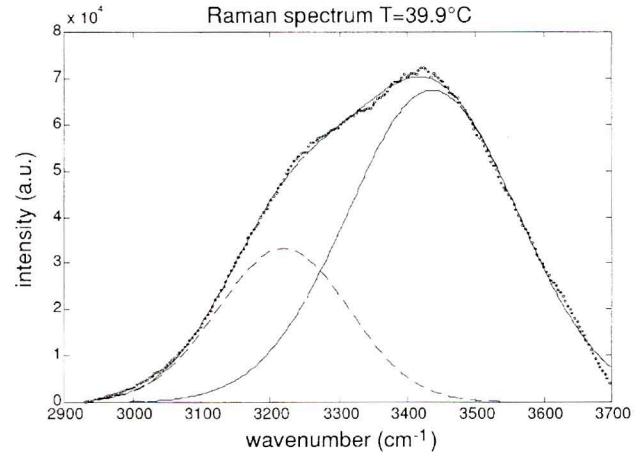


Fig. 3 - Two Raman spectra at different temperatures and their corresponding fittings with two gaussian components: (a) Raman spectrum at  $T=5.0^\circ\text{C}$ , (b) Raman spectrum at  $T=39.9^\circ\text{C}$ .

## 2. FIELD EXPERIMENTS

Field experiments were carried out during an oceanographic campaign in the Tyrrhenian Sea from 3 to 10 September 1991 aboard the National Research Council oceanographic ship (o/s) “*Minerva*”. During field experiments both water Raman and fluorescence spectra in different spectral bands (ranging from 300 nm to 800 nm) were detected by a LIDAR system. This set of spectra was detected every 30 minutes during the 24 hours all through the route of the research vessel, during navigation as well. Moreover, some predetermined measurement stations were visited.

The campaign route is shown in Figure 5 where the full points indicate the measurement stations: particularly, the stretch between the north-eastern coast of Sardinia and Montecristo Island reveals interesting biological features because of a whirlpool which may bring about temperature variations. In this area water column temperature was *in situ* measured at the stations with a bathythermograph. Simultaneously, subsurface water Raman spectra were detected with the LIDAR system.

### 2.1 Instrumentation

The LIDAR system used during the field campaign is the high-resolution fluorescence LIDAR system (FLIDAR 3<sup>®</sup>), designed and built at IROE-CNR (Cecchi *et alii*, 1992). Although this system is mainly devoted to fluorescence measurements, it is used as well to detect the Raman spectrum of the water column with a high spectral resolution (12 cm<sup>-1</sup>). The whole equipment is mounted into a van (FIAT, Ducato Maxi) which permits an easy operation in the field.

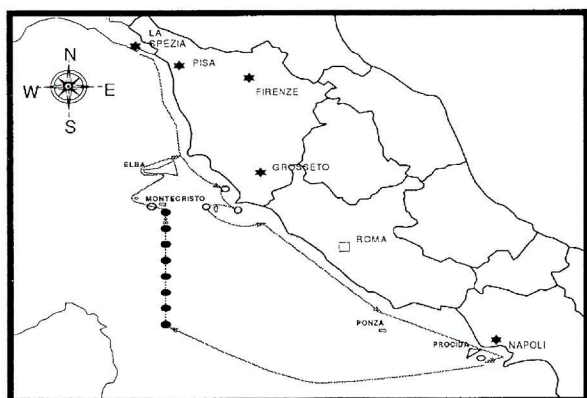


Fig. 5 - Oceanographic campaign route: the full points between the north-eastern coast of Sardinia and Montecristo Island indicate the measurement stations.

### 2.2 Oceanographic campaign and measurement conditions

The van containing the equipment was set on the main deck of the o/s “*Minerva*” and the laser beam was deflected into the water by a 45° mirror extending out from the ship railing. The mirror was placed so as to avoid water turbulence caused by the ship motion.

The excitation source used to detect the Raman signal is an excimer laser (XeCl, 308 nm) with a peak power of 3 MW. At this wavelength the penetration depth is still good with an attenuation length in clear oceanic waters of about 26 m (Smith and Baker, 1981). Since Raman cross section is proportional to the fourth power of source frequency, the Raman signal intensity is enhanced using UV excitation. Moreover, the 308 nm excitation implies that the broad fluorescence band of suspended or dissolved substances is very low in the spectral region affected by the water Raman signal (344 nm with this excitation wavelength), at least for clear water such as those considered in this work. Anyway, this fluorescence band can be easily evaluated (and then subtracted) with a high resolution detection system.

Water column temperature profiles were carried out with a bathythermograph down to 60 meters. The instrument contains a platinum thermometer with an accuracy of 0.01°C. The temperature shows a nearly constant value until a depth of about 15 m is reached. This behaviour is common to all the profiles determined at the measurement stations made between the northeastern coast of Sardinia and Montecristo Island.

The diffuse attenuation coefficient  $k_d$  for oceanic waters at 308 nm (laser wavelength) and at 344 nm (Raman signal wavelength) is 0.116 m<sup>-1</sup> and 0.0637 m<sup>-1</sup> respectively (Smith and Baker, 1981). The coefficient  $k_d$  in fact depends considerably on water turbidity. The values directly measured during the field campaign at 350 nm and longer wavelengths are higher than the ones published for oceanic waters: for example, the directly measured diffuse attenuation coefficient at 350 nm is 0.124 m<sup>-1</sup> (measurement station near Cala Maestra, Montecristo) while for oceanic waters at the same wavelength is 0.0530 m<sup>-1</sup> (Smith and Baker, 1981). Comparing these values, an attenuation length at 308 nm not longer than 15 m can be inferred.

Raman spectra were collected integrating the signal obtained on 200 laser pulses at a repetition rate of 1 pps. An especially implemented acquisition mode permits an automatic background subtraction between each laser pulse and the following one. The gating works at a double frequency with respect to the laser repetition rate. The gating parameters and the distance from the target were such that the system could at most monitor a 10 m water column.

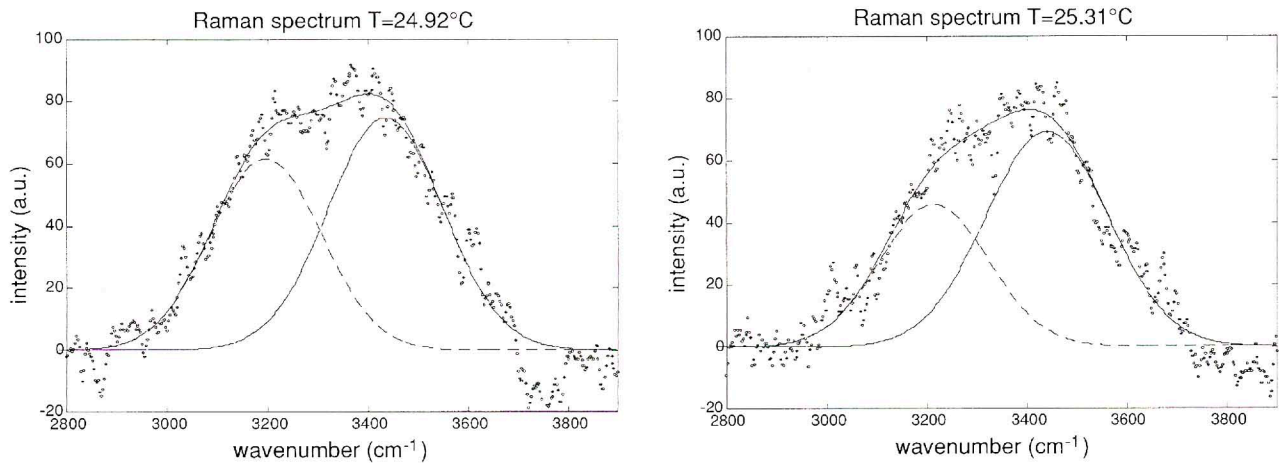


Fig. 6 - Two remote Raman spectra and their corresponding fittings with two gaussian components: (a) Raman spectrum at  $T=24.92^{\circ}\text{C}$ , (b) Raman spectrum at  $T=25.31^{\circ}\text{C}$ .

A long pass optical filter (transmitting 50% at 320 nm) was placed at the telescope output to cut off the backscattered laser line.

### 2.3 Results and discussion

Remote Raman spectra of sea-water column were detected at eight measurement stations, where the ground truth temperature profiles were *in situ* measured together with the salinity profiles. Both these profiles have a depth resolution of 20 cm and an accuracy of  $0.01^{\circ}\text{C}$  and of 0.01 ppt respectively for temperature and salinity measurements. While the column mean temperature varies between the different stations, the salinity values are almost constant  $38.3 \pm 0.1$  ppt). All the spectra were fitted with two gaussian components, using the same method developed for the laboratory data. In Figure 6 two remote Raman spectra at different temperatures are presented together with their fits. Also these spectra roughly show two bands similar to the ones observed in the laboratory spectra, but the intensity variation vs. temperature is more evident.

Figure 7 shows the ratios between the normalized intensities of the two gaussians as a function of temperature. These data were fitted with a linear curve using the least squares method. The reported temperatures were obtained averaging the temperature values of the water column down to a depth of 10 m. Actually, in the first 10 m layer negligible temperature variations occurred (at most  $0.02^{\circ}\text{C}$ ), as also salinity variations.

Comparing these results with those obtained in the laboratory a considerable increase in sensitivity is soon noticed. In this case small temperature variations are detected better than expected from the laboratory results. This sensitivity

increase could be introduced by a parametric amplification of the Raman signal, which, even being a non-linear process, might be considered linear in a small range of temperature values, such as those detected. Actually, the measurement conditions were such that the Raman signal was backward collected. The excitation source had a considerable peak power density due to the use of a pulsed ultraviolet laser (about  $0.4 \text{ MW}/\text{cm}^2$  at 308 nm). To strengthen this hypothesis the Raman spectra show two more pronounced peaks in comparison with the laboratory spectra. This is one of the feature of stimulated Raman spectra (see for instance Rahn *et alii*, 1969). However, the performed measurements are really few and besides, the errors relative to the ratios are still too high to infer such a conclusion. Anyway, work is in progress to verify the real potential of such a method. If these results are confirmed by further sets of measurements, a new method could be introduced to achieve a higher sensitivity for temperature remote measurement.

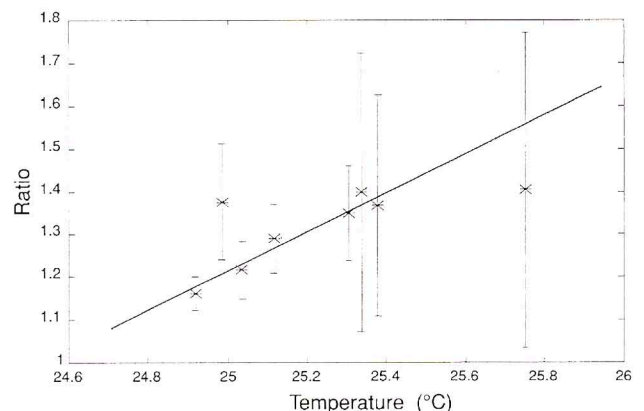


Fig. 7 - Intensities ratio as a function of the column mean temperature.

### 3. CONCLUSION

A water temperature measurement technique was studied both in the laboratory and in the field by means of water Raman spectrum analysis.

Laboratory experiments on a synthetic sea water sample have pointed out temperature sensitive parameters of Raman spectra which can be suitable for remote sensing applications, such as the ratio between the normalised intensities of two gaussian curves.

Remote sensing experiments have shown the usefulness of a high spectral resolution LIDAR system to detect subsurface water temperature. High-resolved Raman spectra were first detected during an oceanographic campaign and analysed by a gaussian fitting procedure, which shows good potential for improving this technique. Moreover, the use of an excimer laser as an excitation source could introduce interesting effects due to a parametric amplification of the Raman signal. The present experimental data are only a first contribution in this direction, which could bring to interesting results for sea remote sensing techniques. Up to now remote sensing methods do not reach such sensitivity levels in the monitoring of water column temperature. In the near future controlled experiments will be carried out to investigate and better define the capability of this effect.

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