Measurement of Water Column Temperature by Raman Scattering

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ABSTRACT

Lidar is the only remote sensing system up to now capable of measuring the water column temperature. This is performed by the analysis of Raman OH-stretching spectrum since temperature change affects its shape.
In this work water Raman spectra obtained in laboratory are presented and discussed. Furthermore an analysis of the behaviour of useful parameters depending on temperature is implemented and suggested as improvement of this technique.

INTRODUCTION

Remote sensing measurement of water column temperature presently can be only performed with Lidar systems. Actually, laser light, chosen at a proper wavelength, penetrates the water volume, in which complete light extinction occurs after hundreds of meters, so depth resolved spectra can be detected as well.
Water temperature Lidar measurements are carried out by means of OH-stretching Raman signal, which is detected in the region of 2900-3900 cm^{-1}. Raman spectrum shows two characteristic bands related to the concentrations of different OH-stretching oscillator classes of water molecule (i.e.: hydrogen bonded and non-hydrogen bonded): so variation of temperature, which these concentrations depend on, affects Raman shape quite considerably (Walrafen et al., 1986).
In this paper water Raman spectra obtained in laboratory are presented and discussed: a low stray-light spectrometer was used to detect the Raman signal of a water sample excited by an Argon ion laser. The laboratory results confirmed the feasibility of water temperature measurements applied to Lidar remote sensing, as already stated by other Authors (Leonard et al., 1979). Furthermore a data elaboration technique is suggested to optimise the sensitivity of this method.

1. MEASUREMENT OF SEA WATER TEMPERATURE

Remote sensing of sea water temperature from aircraft and satellite is presently performed by means of scanning radiometers or image spectrometers operating in the thermal infrared or microwave regions of the electromagnetic spectrum. Even if the accuracy of the measurement is high (0.1 °C), the detection is limited to the "skin temperature" of water as the penetration into the water at these wavelengths is very low.
Since the visible is the only part of the electromagnetic spectrum which gives appreciable penetration depths (Smith and Baker, 1981), an optical technique is very attractive to measure temperature along a water column.

2. EXPERIMENTAL PROCEDURES

The aim of these laboratory experiments was to collect a set of results able to be used as ground truth data during lidar campaigns: so the procedure adopted during the experiments reduces the utilisation of parameters hard to be controlled during field experiments such as absolute intensities and polarization.
The experimental set up is shown in fig. 1: the excitation source was a 0.6 W cw Argon ion laser operating at 514,5 nm and the other main parts will be described hereafter.

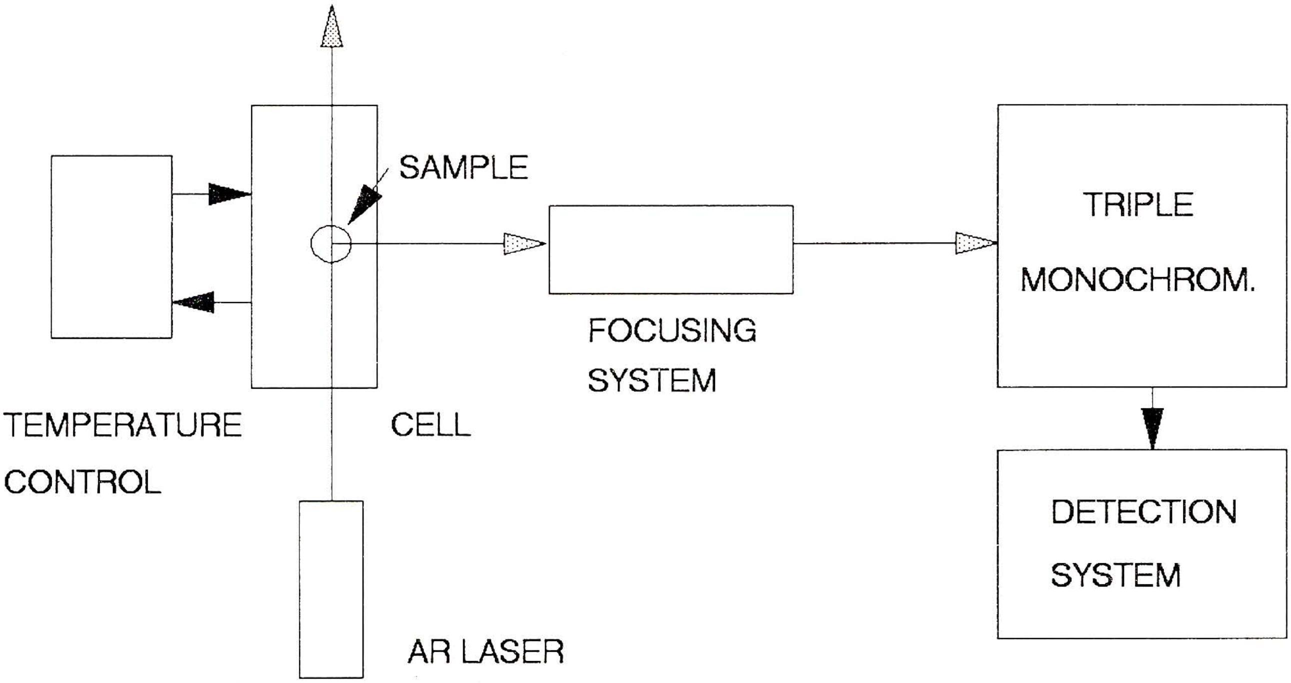

Fig. 1 - Block diagram of the experimental set-up.

2.1 Detection system

The scattered radiation was collected at 90° with respect to the excitation beam and handled with a proper optics in order to maximize the signal at the entrance slit of a triple monochromator (TRIPLEMATE 1877 SPEX, 600 mm focal length) with a very low stray light level (10^{-14} at 10 bandpass from the excitation line). This kind of monochromator is certainly unsuitable as field instrument but here gives the capability to collect the signal of a very little sample.
The spectrum at the monochromator output was detected by a 512 channels intensified linear diode array (EG&G Mod PDA 1463), part of an optical multichannel analyser (EG&G, OMA 2000). This detection system is quite similar to that utilised in the FLIDAR-3 fluorescence lidar (Cecchi et al., 1991).

2.2 The sample

A sample of high purity water was maintained in a sealed phial in order to avoid contamination. The phial was plunged in a thermostatic bath also made of water; the temperature control had a sensitivity of 0.1 °C. During the experiments the sample temperature varied from 2.5 °C to 40 °C. The optical collection system was designed so as to concentrate the focal region within the sealed water sample.

3. RESULTS AND DISCUSSION

Raman spectra from liquid water were fitted with three Gaussian curves (fig.2.a): the number of Gaussian curves adopted to fit spectra corresponds to a compromise between the expectation of preserving the maximum information with a low number of parameters and, on the other hand, the requirement of a good fitting. In Figure 2.b the detected spectrum and the corresponding fit obtained adding the three curves are reported: although there is not a theoretical support to prefer a Gaussian fit, the agreement between experimental data and fitted curve is satisfactory. Here a mean square deviation of about 1.4% was estimated for all the spectra. Even if three Gaussians are necessary to properly reproduce the detected spectra, it turns out that only the two major contributions show a sizable temperature dependence, while the third one (i.e. the highest frequency component) does not change significantly. Therefore, in the following only the parameters

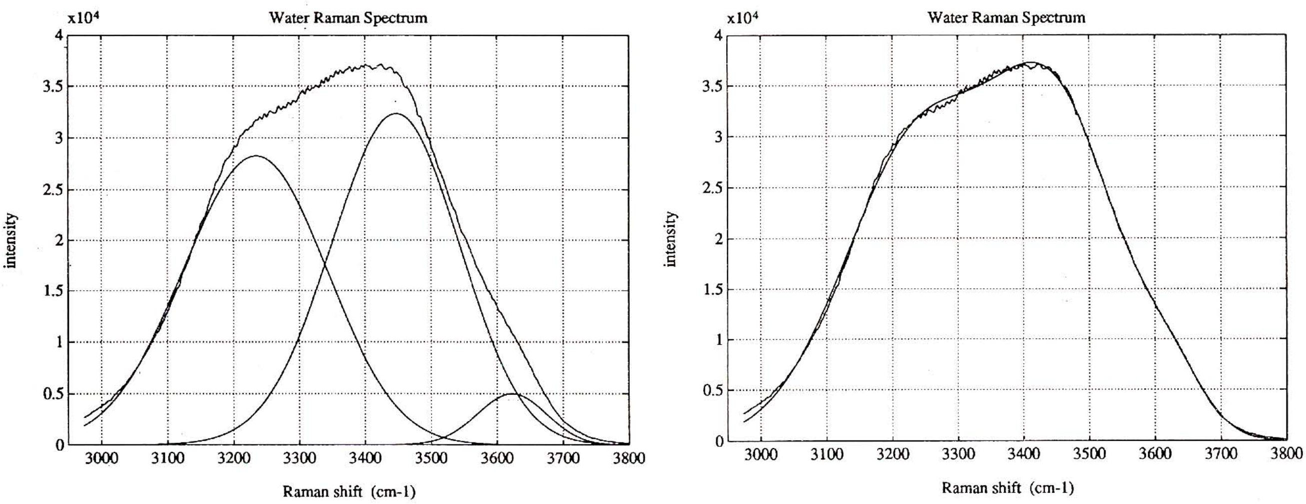

Fig. 2 - a) Water Raman spectrum and its three Gaussian components. This spectrum was taken at T= 10°C; b) The same water Raman spectrum and the corrisponding curve obtained adding the three Gaussians.

related to these two temperature dependent components will be reported and discussed.

Figure 3 puts in evidence the modification upon temperature of the Raman spectra: the general behaviour of the curves shows that the low frequency part of the spectrum (3000-3400 cm^{-1}) decreases with temperature, while the high frequency one (3400-3800 cm^{-1}) increases.

Both the position of the centres and the ratio between the intensities of the two main Gaussian curves at a given temperature were analyzed as a function of temperature: in particular, it results that the latter is the most useful parameter for an accurate temperature determination.

Figure 4 shows the ratio between the intensities of the two Gaussian curves, plotted versus temperature, and the fitting of the data with a linear equation. The slope of the line, in terms of the change of the ratio for a variation of 1 °C, is about 1%.

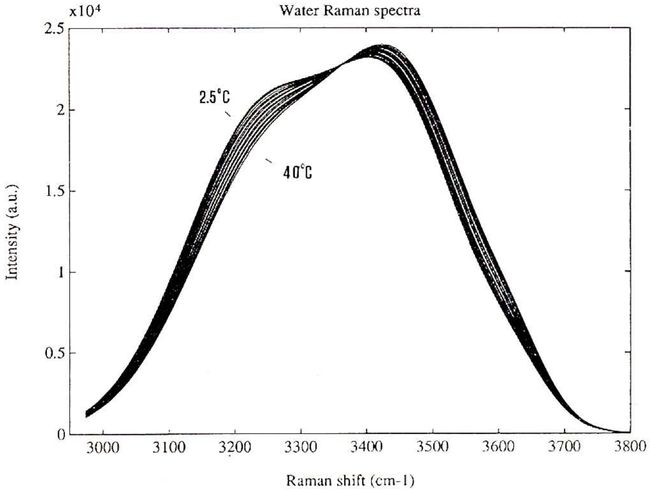

Fig. 3 - Water Raman spectra taken at different temperatures (from 2.5 °C to 40 °C).

However, in order to test the accuracy of the method, the present experimental data have been used to determine the temperature of the sample. The average deviation from the true temperature is @ 0.5 °C in the full range from 2.5 °C to 40 °C.

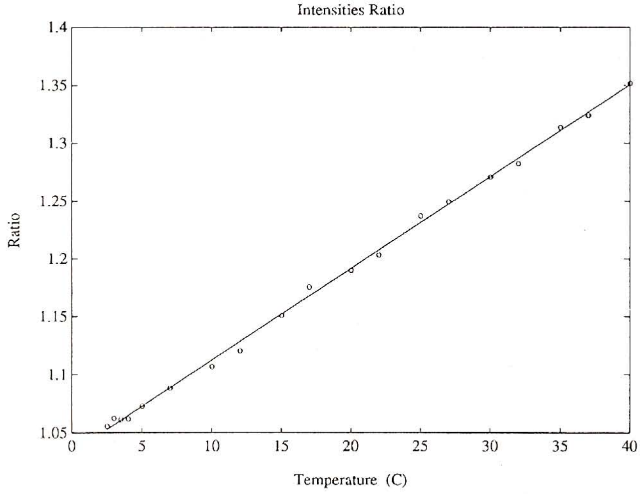

Fig. 4 - The ratio between the intensities of the two main Gaussian curves plotted versus temperature.

The peak positions as well can be used to obtain an independent determination of the sample temperature. Figure 5 shows the behavior of these quantities when the peak positions at 22 °C are taken as a reference. It can be noted that both peaks move in the same direction as temperature changes, therefore a temperature determina-

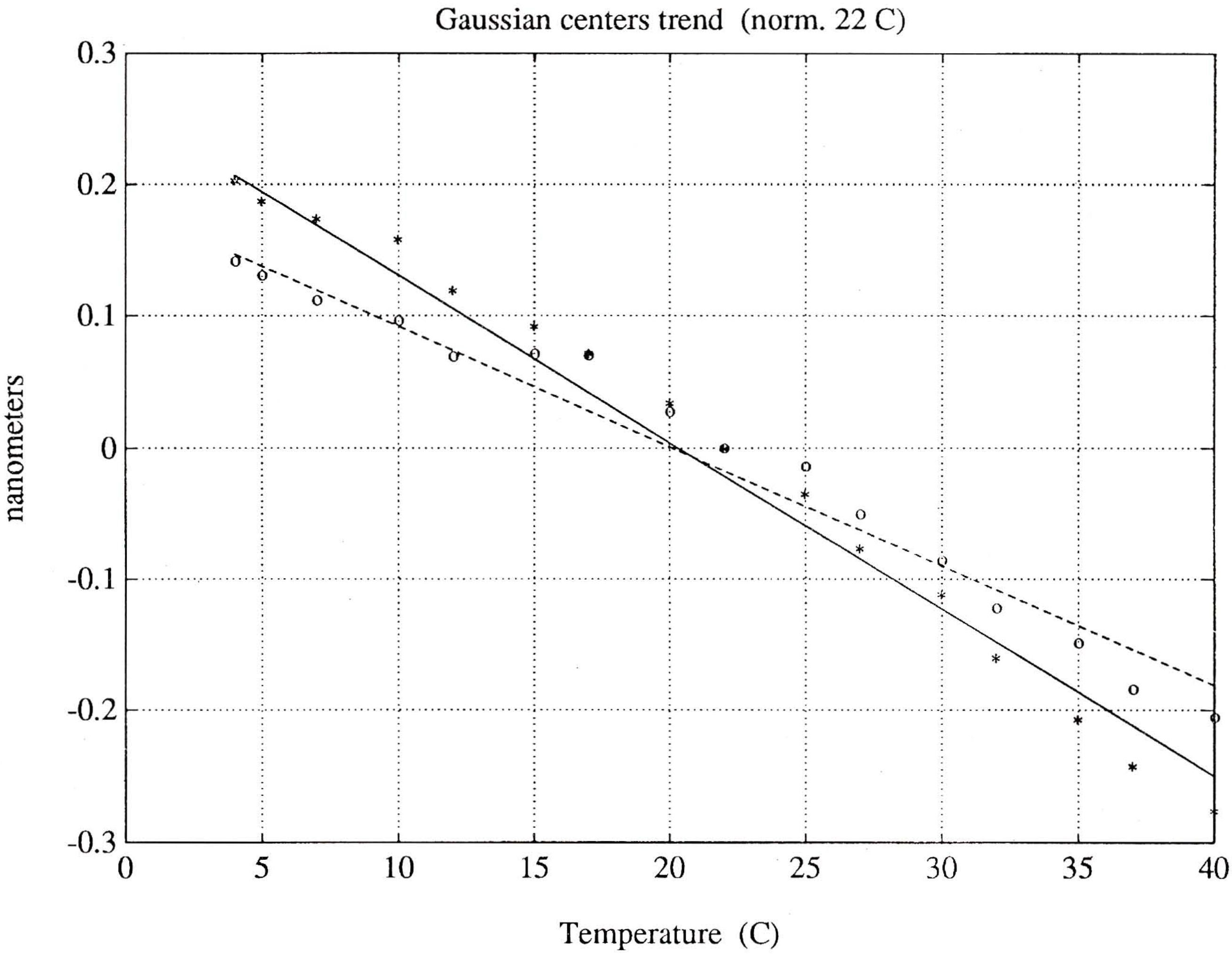

Fig. 5 - The behavior of the Gaussian centers as a function of temperature. All the values are normalized to the Gaussian centers at a temperature of 22 °C.

tion based on these parameters appears more bound to an absolute frequency calibration of the spectrometer. However, this method can be used to obtain an independent determination which can be used to increase the accuracy of the temperature measurement.

CONCLUSIONS AND FUTURE TRENDS

The first laboratory results show a good potential of a three Gaussian fitting for the determination of temperature from water Raman spectra. In the temperature range of interest a good linear fitting was found for the ratio between the intensities of the two main Gaussian curves as a function of temperature. For pure distiled water a sensitivity of about 1% was found.

Furthermore the behaviour of other parameters (such as the Gaussian centre shift) was analysed and suggested to improve this method.

The laboratory experiments will be extended in the near future to sea water samples, both synthetic and natural; moreover another set of measurements under controlled conditions will be performed with field instruments to be related to the laboratory results.

A first FLIDAR-3 field campaign, carried out on this Lidar application, is expected at the end of August 1991.

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