Accuracy of remote sensing of water temperature by Raman spectroscopy

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We present an experimental study of the Raman spectrum of pure and synthetic seawater with respect to its salinity and temperature dependence. Experiments made in the laboratory with both cw and pulsed excitation yield information on the limits and applicability of the technique in actual experiments in the field. We have also performed an experimental analysis to determine the presence of stimulated Raman scattering and its influence on the temperature dependence of the spectrum. © 1999 Optical Society of America

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1. Introduction

The Raman spectrum of liquid water in the 3000–4000-cm^{-1} region, which originates from symmetric and antisymmetric OH stretching vibrations, is present in the form of a broad structured band with several spectral components.[1–3] Liquid water has a complex structure owing to the existence of intermolecular hydrogen bonding and electrostatic interactions. This structure is not rigid because of the flexibility of the hydrogen bond and its relatively low energy. Therefore the structure is sensitive to temperature and to the presence of ions in solution.[3–6] These properties make liquid water attractive as a medium for remote sensing of water temperature, as was shown by Leonard *et al.* in a study of the subsurface Raman spectrum of water and in a subsequent extension of the study to open-sea temperature measurements.[7,8] Recently high-resolution Raman scattering experiments for the monitoring of water column temperature were carried out in the Tyrrenian sea by Cecchi and Raimondi.[9]

In spite of the fact that the method was proposed in the 1970's, few experiments have been made in the field, because, owing to environmental constraints, the measurements have to be performed with pulsed laser sources. Moreover, the comparison of the laboratory cw results with the pulsed field measurements is not completely satisfactory.[9] In this paper we present an experimental study of the Raman spectra of pure water and seawater with respect to salinity and temperature dependence in both pulsed and cw experimental conditions. We investigate the presence of stimulated Raman scattering and its influence on the temperature dependence of the spectrum.

2. Results Obtained with cw Excitation

We prepared synthetic seawater by dissolving in deionized water different amounts of a salt mixture whose composition is the following:

$$Na^+, 28.4\%; K^+, 2.2\%; Ca^{2+}, 1.2\%;$$
$$Mg^{2+}, 4.1\%; Cl^-, 47.4\%; SO_4^{2-}, 16.7\%. \quad (1)$$

The sample was contained in a glass cell (10 × 10 mm) thermally stabilized within 0.1 °C. The cw Raman spectrum of water was measured in a 90° scattering geometry. $X(Y - YX)Z$ polarization[10] was used, with a polarization scrambler placed before the entrance slit of the monochromator. The Raman spectrum was excited by an argon-ion laser 514.5-nm line with a power of 60 mW at the sample. The scattered radiation was analyzed with a 1-m focal-length double monochromator equipped with 1800-
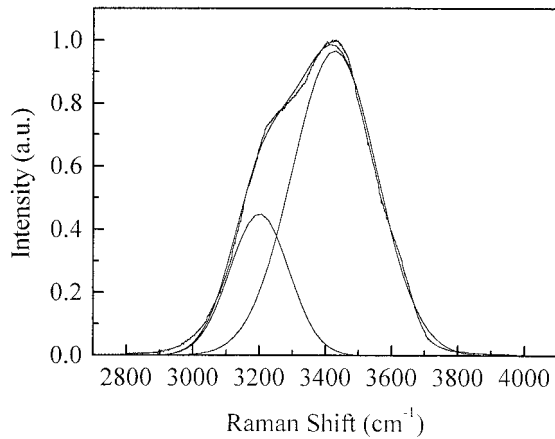
Fig. 1. Typical Raman spectrum obtained with cw excitation superimposed upon fits based on a two-Gaussian model. The two Gaussians are also shown.
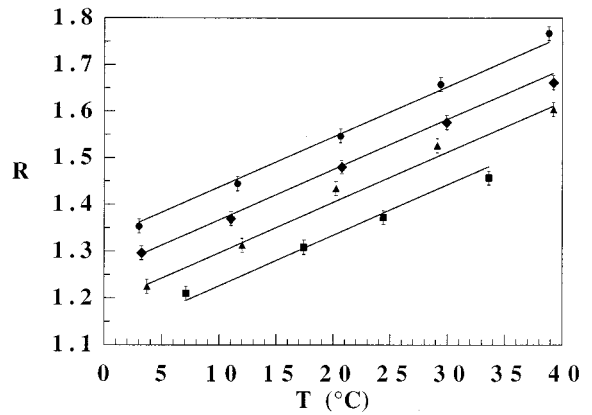

Fig. 2. Ratio R obtained from the measured spectra with cw excitation, as defined in the text [Eq. (2)], versus temperature. Solid curves, fits with Eq. (3) and parameters (4). Each curve corresponds to a different value of the salinity s: from top to bottom, $s = 38, 26, 13, 0$ g/L.

grooves/mm holographic gratings and detected by a CCD camera.

The investigation of the Raman spectrum aims to measure the dependence of a spectral marker on the temperature and salinity of the water sample. We have chosen to study the scattered light by unpolarized detection because both polarization components, perpendicular and parallel with respect to the laser polarization, change with temperature; we also chose to employ the usual field experimental setup. A typical spectrum is shown in Fig. 1; superimposed upon it is a fit with two Gaussian profiles. A larger number of Gaussians can be used, which will result in a better fit; nevertheless, we did not find that they provided a clear improvement in sensitivity or accuracy in the determination of our marker. We recorded the Raman spectrum of water samples with different salinities (0–38 g/L) and temperatures (3–40 °C), and we extracted as a marker the following adimensional expression:

$$R = (H_1/W_1)/(H_2/W_2), \qquad (2)$$

where H_i and W_i are the height and the width of the Gaussians and $i = 1, 2$ indicates higher- and lower-frequency bands, respectively. The choice of this marker was prompted by results of a previous study.[9] We also tried different markers based on the same parameters, but it seems that the marker described by Eq. (2) is most suitable for our purposes. We then fitted the marker behavior with the two-variables expansion

$$R = A + B(T - T_0) + C(s - s_0) + D(T - T_0)^2$$
$$+ E(T - T_0)(s - s_0) + F(s - s_0)^2, \qquad (3)$$

where s is the salinity in grams per liter, T is the temperature in degrees Celsius, and $s_0 = 19$ g/L and $T_0 = 21$ °C are two constants. As a result, the non-linear terms in s and T are negligible, and therefore

we use here a fit with only three parameters, A, B, and C:

$$A = 1.451 \pm 0.004,$$
$$B = (1.08 \pm 0.03)\ 10^{-2}\ °\text{C}^{-1},$$
$$C = (5.6 \pm 0.2)\ 10^{-3}\ 1/G. \qquad (4)$$

In Fig. 2 the experimental results with relative error bars and fitted curves are shown. It is important to note that overall agreement is obtained with only three parameters. The use of the method presented here is not suitable for simultaneous determination of both salinity and temperature.

3. Results Obtained with Pulsed Excitation

The reason for performing a study of the temperature marker with a pulsed experiment is twofold: to be close to actual experimental conditions in the field, in which pulsed excitation was used, and to investigate the discrepancies between cw and pulsed results that have been reported in the literature. For this purpose we also studied the effects of the presence of stimulated Raman scattering, which in principle can strongly alter the detected spectrum with respect to the weak-field (cw) measurement. The laser beam ($\lambda = 354.7$ nm, 6-ns pulse duration, third harmonic of a pulsed Nd:YAG laser, linearly polarized) passed through a 1-m-long cell of deionized water ($s = 0$) thermally controlled within 0.1 °C in the 17–26 °C range. Backscattered light, collected by a pierced mirror, was focused onto the entrance slit of a 0.25-m focal-length spectrometer. The entire spectrum of interest was detected by a gated intensified optical multichannel analyzer and averaged over 500 laser pulses. The analyzer was provided with two parallel arrays of photodiodes. We used these two arrays to detect the light scattered on axis with respect to the laser beam and off axis at the same time. We chose to determine the marker from the $P + S$ [$X(Y, YZ)X$ geometry] spectrum because it is the quantity
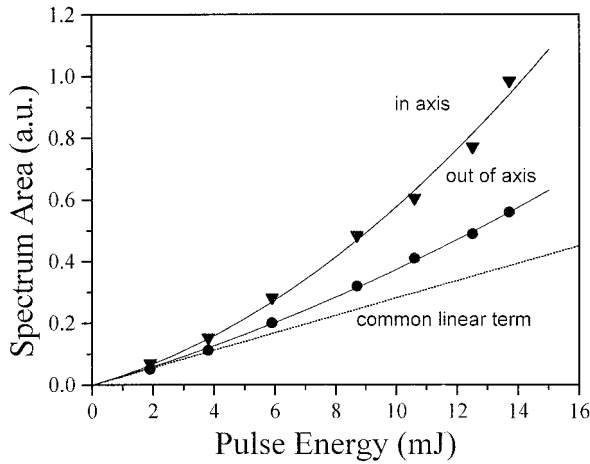
Fig. 3. Spectrum area versus pulse energy: triangles, detection with an aligned photodiode array (on axis with respect to the laser beam); circles, detection with a misaligned photodiode array (off axis to the laser beam). Corresponding curves, quadratic fits to the pulse energy. The data are normalized to have the same linear dependence on the pulse energy (dotted curve). Assuming that both the temporal and the spatial beam profiles are rectangular, the intensity that corresponds to 10 mJ is 18 MW/cm^2.

Fig. 4. Ratio R obtained from the measured spectra with pulsed excitation versus temperature ($s = 0$). Solid curve, linear fit of the data.

observed in field measurements. We performed two series of measurements: changing pulse energy with fixed water-cell temperature and changing temperature with fixed energy. The first type of measurement was done to investigate the presence of stimulated scattering that may be present in pulsed field experiments and may cause discrepancies with the cw laboratory results. In Fig. 3 we show the integrated intensities of the Raman spectra versus laser energies at $T = 19.1\,°C$ for aligned and non-aligned detection (made with the two photodiode arrays). The solid curves are fits to quadratic expressions in the pulse energy; the data are normalized to have equal linear contributions, as shown by a dotted curve. We note that the aligned measurement has a more pronounced nonlinear contribution than does the misaligned measurement. The different behavior of the two curves leads us to ascribe the quadratic term to stimulated scattering. In fact, the beam detected by the aligned array travels inside the volume where the laser is present, whereas the other beam travels mainly outside this volume, making the stimulated process less efficient. To quantify the effect of the stimulated scattering process on the temperature marker we calculated the ratio R for the spectra corresponding to the points of Fig. 3. The values obtained did not show any pronounced energy-dependent behavior. The mean value of R for the aligned set of spectra is 1.49 ± 0.02; that for the nonaligned set of spectra is 1.51 ± 0.04. The two results are compatible within the experimental dispersion. We find that, for the pulse intensity range used in our measurements, the effect of the stimulated process does not alter the value of the temperature marker.

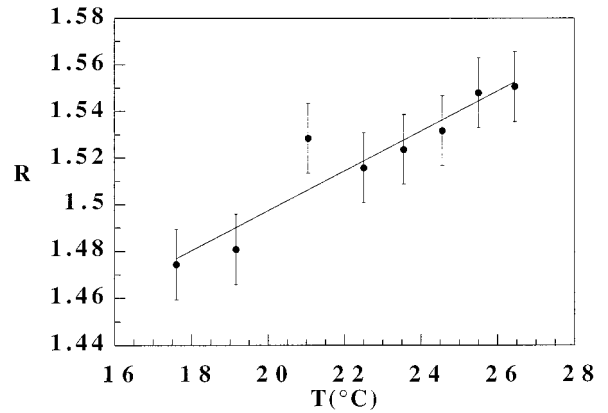The second series of measurements was aimed at the determination of the marker as a function of temperature (always with $s = 0$). In Fig. 4 we show the temperature marker for spectra made to detect the aligned part at 10 mJ of pulse energy. The fit was done with the linear expression

$$R = A' + B(T - T_0),\qquad(5)$$

where $A' = A - Cs_0$ [see Eq. (3)]. The same evaluation was repeated for the nonaligned measurement:

$$A'(\text{aligned}) = 1.506 \pm 0.004,$$
$$B(\text{aligned}) = (8.7 \pm 1.3)\ 10^{-3}\ °C^{-1};$$
$$A'(\text{not aligned}) = 1.518 \pm 0.009,$$
$$B(\text{not aligned}) = (13 \pm 3)\ 10^{-3}\ °C^{-1}.\qquad(6)$$

We note that the values are consistent within the experimental uncertainty; again the presence of stimulated Raman scattering does not seem to alter the temperature marker significantly.

The results obtained with cw and pulsed excitation show that the variation of the spectrum with temperature and salinity can be summarized in an effective marker. As expected, the uncertainties in the parameters are larger for pulsed excitation. For the temperature dependence of R, the cw and pulsed results are consistent within experimental error. The difference in the constant part of R for cw and pulsed results reveals that the absolute determination of the temperature from the spectrum can be critical.

4. Conclusion

We have performed a study of the Raman spectrum of water as a function of temperature and salinity in cw excitation. Changes in the spectrum from these parameters can be summarized by an effective marker. We also performed an experiment with pulsed excitation, looking at the temperature dependence of the marker; an analysis of the effects of stimulated Raman scattering was made. In brief, the results of our experiment are the following: The marker is a linear function of salinity and temperature. The re-

sults of the pulsed excitation measurements show that, even if the integrated spectrum can be a nonlinear function of the excitation energy pulse, the temperature marker does not depend on the energy of the pulse in our range of measurements. The temperature dependences of the marker for the cw and for pulsed results are consistent within experimental uncertainties. The sensitivity of the method is such that calibration of the specific experimental setup is needed.

In conclusion, we have studied the application of Raman scattering for determination of temperature or salinity of water. The experiments made in the laboratory with both cw and pulsed excitation give information on the limits and applicability of the technique in actual experiments in the field.

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10. In the notation $X1(X2, X3)X4$, $X1$ denotes the laser axis, $X2$ the laser polarization, $X3$ the collecting polarization, and $X4$ the collecting direction.