

RAMAN SPECTROSCOPY MEASUREMENT OF CH₄ GAS AND CH₄ DISSOLVED IN WATER FOR LASER REMOTE SENSING IN WATER

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ABSTRACT

We examined the applicability of Raman spectroscopy as a laser remote sensing tool for monitoring CH₄ in water. The Raman technique has already been used successfully for measurements of CO₂ gas in water. In this paper, considering the spectral transmittance of water, third harmonics of Q-switched Nd:YAG laser at 355 nm (UV region) was used for detection of CH₄ Raman signals. The Raman signal at 2892 cm⁻¹ from CH₄ dissolved in water was detected at a tail of water Raman signal.

1 INTRODUCTION

Lidar (light detection and ranging) is a very promising technique for monitoring the vast seafloor, and it is very useful for exploring mineral and natural gas deposits on a seafloor, monitoring the environmental change and working condition within submarine industrial facilities [1-4]. Although most lidar techniques can be applied to atmospheric sciences [5], their applications in water are not straightforward, because water is a strong light absorber showing relatively high transmission only in the shorter wavelength region from UV to Green spectral range [6]. For example, CO₂ gas is usually detected by infrared absorption methods [7, 8], but conventional infrared absorption spectroscopy is not suited for sensing gasses in water due to strong IR absorption [9]. Therefore, we proposed Raman lidar using UV-Green laser with relatively high transmission in water.

We reported on progress toward developing a technique for the underwater remote detection of gases in water using Raman lidar in our previous papers [1-4]. We used CO₂ gas to demonstrate our approach because it is easy to handle. Firstly, its effectiveness was demonstrated with remote identification of CO₂ dissolved in water in a glass bottle located 20 m away [1]. Next, applications of our approach to the quantitative analysis of the

CO₂ concentration in water were presented for comparison with CO₂ dissolved in water and CO₂ bubbles [2, 3]. Also, the effect of seawater on CO₂ Raman spectra has been evaluated [4].

In this paper, we report measurements of CH₄ as well as CO₂ dissolved in water by laser Raman spectroscopy. We used the laser at 532 nm as the light source in the previous experiments. However, the CH₄ Raman signal (2892 cm⁻¹) excited by a 532 nm laser is distributed in the wavelength range at around 628.7 nm, where the spectral transmittance of water is not good [6]. Therefore, in this study, we utilized the 355 nm laser source which has lower attenuation in water compared with the 532 nm laser. The Raman signal at 2892 cm⁻¹ from CH₄ dissolved in water was detected at a tail of water Raman signal using the 355 nm laser source. Thus, we can apply our methods to CH₄ as well as CO₂ gases. We expect that the submarine Raman lidar application will significantly improve the monitoring the vast seafloor.

2 EXPERIMENT

A schematic diagram of the Raman spectroscopy is given in Fig. 1. We use a standard Q-switched Nd:YAG laser (Continuum, Surelite) operating at its third harmonic wavelength of 355 nm. This laser generates a pulse-width of 10 ns and a pulse energy of 60 mJ at 10 Hz repetition rate. The laser output power is variable by the combination of half-wave plate ($\lambda/2$) and a polarizer.

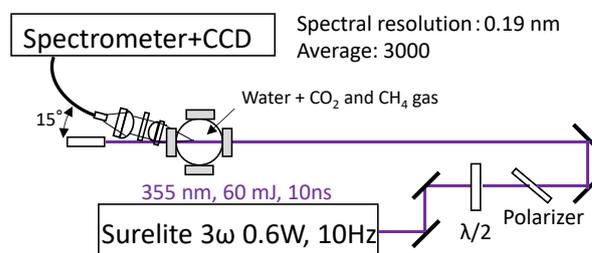


Figure 1 Schematic diagram of Raman spectroscopy experimental setup

The gas-water mixtures were realized by bubbling the CO₂ and CH₄ gases into the water in a high pressure chamber. This chamber is designed to withstand 10 MPa pressure, which is equivalent to a depth of 1000 m in the ocean. This chamber has four sapphire crystal windows and a rotation blade. The high-speed agitation by the rotation blade has efficiently achieved the equilibrium between the pressure in the water and the pressure in CO₂ and CH₄ gases. The pressure is monitored with both analog and digital pressure gauges. Also, a thermocouple located in water provided a measure of the water temperature.

The chamber is initially filled with about 180 mL deionized water, and CO₂ and CH₄ gases are introduced from a gas cylinder into the water. Each of the equilibrium steps is carried out for 5 minutes at about 22.5 degrees Celsius with rapid agitation (1000 rpm).

The Raman signals from samples are collected using an achromatic lens at an angle of 15° from the forward direction of the laser beam. This design provides a longer optical path length than a conventional detection geometry at 90°, offering an order of magnitude increase in Raman scattering intensity. After passing through the edge filter at 355 nm, the Raman signal is coupled into an optical fiber bundle by using an achromatic lens. The collected Raman signal was delivered to a spectrometer (Acton, SpectraPro-2300i) equipped with a thermoelectrically cooled charge-coupled device (CCD) camera (Princeton Instruments, PIXIS 400).

3 RESULTS AND DISCUSSION

Figure 2 shows Raman spectra of CO₂, CH₄ gases and CO₂, CH₄ dissolved in water. These Raman spectra were offset vertically for better visualization. The exposure time was 90 ms. The accumulation number was 3000 and it was repeated 5 times in each case. The entrance slit width of the spectrometer was set to 20 μm and the spectral resolution of this system was estimated to be 0.19 nm.

Figure 2(a) shows typical spectra of CO₂, CH₄ gases and CO₂, CH₄ dissolved in water at around 1 MPa. The broad spectra at 1635 and 3405 cm⁻¹ are mainly the H₂O Raman signals detected in both samples of CO₂ and CH₄ dissolved in water.

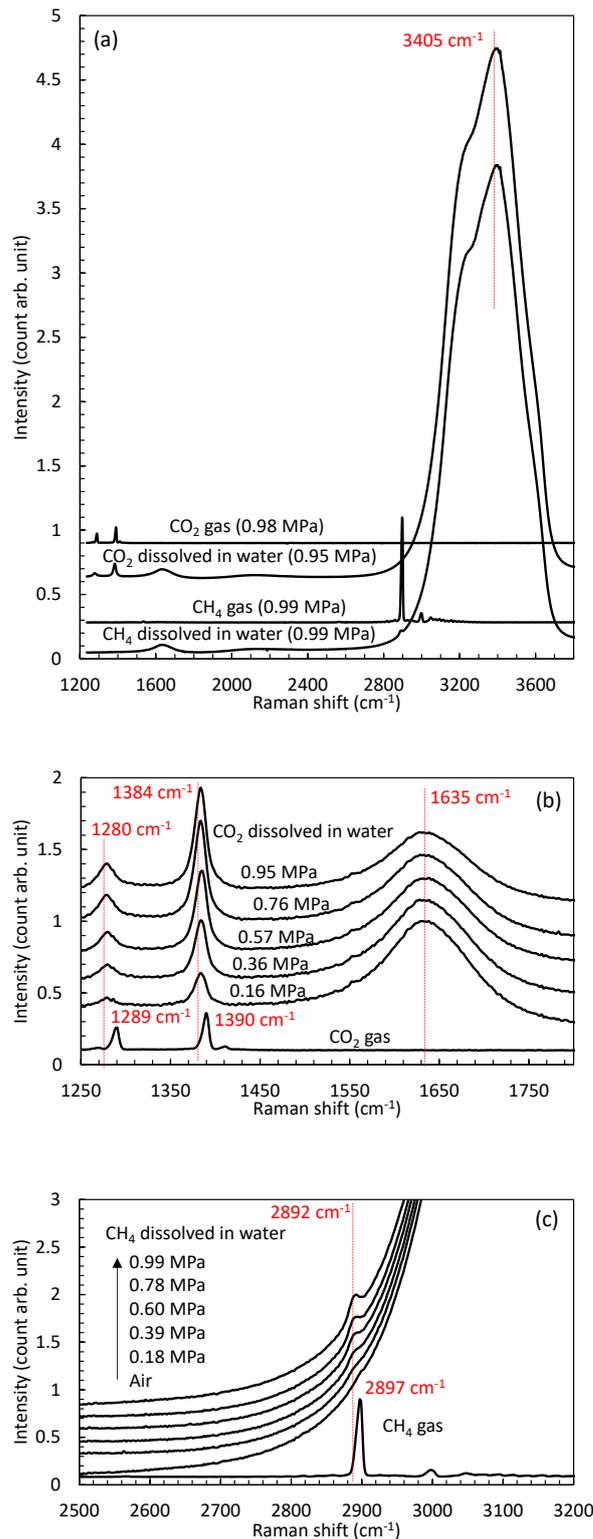


Figure 2 Raman spectra of CO₂, CH₄ gases and CO₂, CH₄ dissolved in water.

These water Raman signals are utilized as an internal standard for evaluating the dissolved gas

concentration. In the CO₂ samples, the relatively sharp bands at 1280 and 1384 cm⁻¹ are CO₂ Raman signals. On the other hand, the spectra of the CH₄ samples have the characteristic peak associated with CH₄ at 2892 cm⁻¹, which is located at a tail of water Raman signal. In the case of CO₂ and CH₄ gases at almost the same 1 MPa pressure, the CH₄ Raman signal is much stronger than the CO₂ Raman signal. This is because the Raman cross section of CH₄ is about five times larger than that of CO₂ [10]. However, in the case of CO₂ and CH₄ gases dissolved in water at almost the same ~1 MPa pressure, the CH₄ Raman signal is much weaker than the CO₂ Raman signal because of the difference in water solubility of these gases.

Figure 2(b) shows the spectra of CO₂ gas at different concentrations dissolved in water. These Raman spectra were normalized at 1635 cm⁻¹ water Raman signal intensity peaks. The relatively sharp bands at 1280 and 1384 cm⁻¹ are CO₂ Raman signals. When CO₂ gas is dissolved in water, the gas phase band position at 1390 cm⁻¹ is shifted to 1384 cm⁻¹ in water. This shift could be attributed to the variation of vibration modes in water.

Figure 2(c) shows the Raman spectra of CH₄ at different concentrations dissolved in water. These spectra have been normalized at ~3405 cm⁻¹ peak value. The Raman signal of CH₄ dissolved in water is centered at 2892 cm⁻¹. When dissolved in water, the band position at 2897 cm⁻¹ shifts to 2892 cm⁻¹ due to the variation of CH₄ vibration modes in water.

Using 355 nm laser, we can detect the Raman signals of CH₄ dissolved in water, but its intensity is very weak. Also, the CH₄ Raman signal is located at a tail of water Raman signal, and it is difficult to distinguish between CH₄ and water Raman signals. However, Raman signals of CH₄ in gas phase is much stronger as shown in Fig. 2(a), and we have confirmed that our methods can be applied to the gas bubbles [3]. Therefore, we can expect that the Raman signals of CH₄ gases in water would be relatively easily detected at the coexistence areas of CH₄ gas dissolved in water and CH₄ bubbles.

4 CONCLUSIONS

We have demonstrated the applicability of Raman lidar technique for 3D laser mapping in water by measuring Raman signals of CO₂ and CH₄ gases in water. The Raman signals at 1280 and 1384 cm⁻¹ from CO₂ in water are detected. The relatively strong Raman signal at 1384 cm⁻¹ is a good candidate for doing Raman lidar measurements in water. Also, the CH₄ Raman signal at 2892 cm⁻¹ was detected at a tail of water Raman signal, but it is very weak due to low water solubility of CH₄ gas. However, Raman signals of CH₄ in gas phase is much stronger, and we can expect that the Raman signals of CH₄ gases in water would be relatively easily detected at the coexistence areas of CH₄ gas dissolved in water and CH₄ bubbles.

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