RAMAN SPECTROSCOPIC MEASUREMENTS OF CO_2 DISSOLVED IN SEAWATER FOR LASER REMOTE SENSING IN WATER

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ABSTRACT

We examined the applicability of Raman lidar technique as a laser remote sensing tool in water. The Raman technique has already been used successfully for measurements of CO_2 gas dissolved in water and bubbles. Here, the effect of seawater on CO_2 Raman spectra has been evaluated. A frequency doubled Q-switched Nd:YAG laser (532 nm) was irradiated to CO_2 gas dissolved in a standard seawater. In seawater, the Raman signals at 984 and 1060-1180 cm^{-1} from SO_4^{2-} were detected, which shows no spectral interference caused by Raman signals derived from CO_2.

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 [1-3]. However, its development is limited almost to atmospheric remote measurements [4], because water is a strong light absorber showing relatively high transmission only in the shorter wavelength region from UV to Green spectral range [5]. For example, CO_2 gas is usually detected by infrared absorption methods [6,7], but conventional infrared absorption spectroscopy is not suited for sensing gasses in water due to strong IR absorption [8]. Therefore, we proposed Raman lidar using 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 [1-3]. We used CO_2 gas to demonstrate our approach because it is easy to handle. Firstly, its effectiveness was demonstrated with remote identification of CO_2 dissolved in water in a glass bottle located 20 m away [1]. Next, applications of our approach to the quantitative analysis of the CO_2 concentration in water were presented for comparison with CO_2 dissolved in water and CO_2 bubbles [2, 3].

In this paper, we report measurements of CO_2 dissolved in seawater by laser Raman spectroscopy. Seawater Raman spectrum has characteristic peaks at 984 and 1060-1180 cm^{-1} from SO_4^{2-}, which does not cause interference by CO_2 Raman measurements. Hence, submarine Raman lidar could be a useful technique for 3D laser mapping of CO_2 leakages in water.

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 second harmonic wavelength of 532 nm. This laser generates a pulse-width of 10 ns and a pulse energy of 100 mJ at a 10 Hz repetition rate. The wavelength of the laser was chosen at 532 nm due to lower attenuation in water.

The gas-water mixtures were realized by bubbling

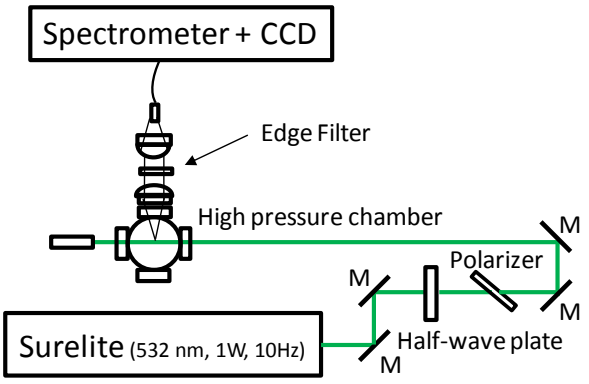

Figure 1. Schematic diagram of Raman spectroscopy experimental setup.

the CO_2 gas 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 CO_2 gas. 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 or IAPSO (International Association for the Physical Sciences of the Ocean) standard seawater (OSIL). After degassing in vacuum for 30 minutes, CO_2 gas is 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 signal from CO_2 in water is collected using an achromatic lens at an angle of 90° to the laser beam. After passing through the edge filter at 532 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 liquid nitrogen-cooled charge-coupled device (CCD) camera (Princeton Instruments, SPEC-10).

3. RESULTS AND DISCUSSION

Figure 2 shows typical spectra of CO_2 dissolved in water and seawater. These spectra have been normalized at ~1645 cm^{-1} peak value after subtraction of the background, and 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 0.23 nm.

The broad spectrum at ~1645 cm^{-1} is mainly the H-O-H bending band detected in both samples. The relatively sharp bands at ~1277 and ~1383 cm^{-1} are CO_2 Raman signals. The relatively strong Raman signal at ~1383 cm^{-1} is a good candidate for doing Raman lidar experiment in water [1]. Also, the water Raman signal at ~1645 cm^{-1} is utilized as an internal standard for evaluating the dissolved CO_2 concentration [2]. On the other hand, the spectrum of the standard seawater has characteristic peaks associated with the SO_4^{2-} of the S-O symmetric stretching mode at ~984 cm^{-1} and anti-symmetric stretching modes from 1060 to 1180 cm^{-1}[9], which do not interfere with the CO_2 Raman spectrum. The dissolved CO_2

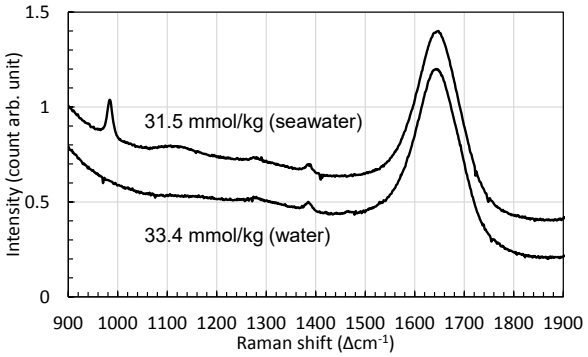

Figure 2. Raman spectra of CO_2 dissolved in water and seawater.

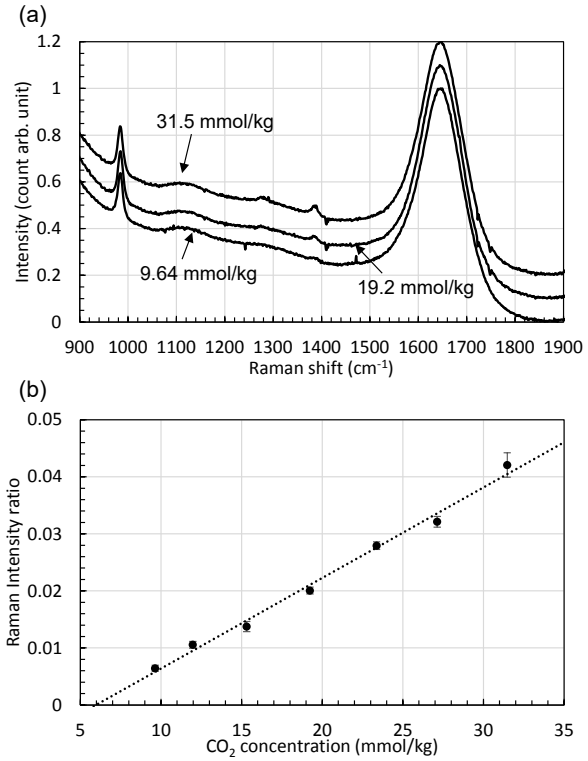

Figure 3. (a) Raman spectra of CO_2 dissolved in seawater at different CO_2 concentrations and (b) dependence of dissolved CO_2 concentration versus CO_2/H_2O Raman bands peak ratio.

concentrations were calculated from the pressure of the chamber using Henry's law [10].

Figure 3(a) shows Raman spectra of CO_2 dissolved in seawater at different dissolved CO_2 concentrations. Raman peak intensity at ~1383 cm^{-1} increased linearly versus increasing dissolved CO_2 concentration. Intensity ratios of CO_2/H_2O Raman signals at ~1383 cm^{-1} and ~1645 cm^{-1} for different CO_2 concentrations are plotted in Fig. 3(b). The error bars were evaluated using the standard deviation of 5 consecutive spectra. Using our current detection system, the spectrum of the dissolved CO_2 concentration at about 10 mmol/kg could be detected. These ratios can be reasonably well fitted by a straight line, however, the fitting line does not pass through the "0" origin. This may be due to the saturated vapor pressure of the gas-water mixture system.

4. CONCLUSIONS

We have demonstrated the applicability of Raman lidar technique for 3D laser mapping in water by measuring CO_2 gas dissolved in seawater. In seawater, the Raman signals at 984 and 1060-1180 cm^{-1} from SO_4^{2-} were detected, showing no spectral interference caused by Raman signals derived from CO_2. The results show that our technique can be applied to an efficient underwater ocean monitoring system.

ACKNOWLEDGEMENT

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