Preliminary Results of H_2O and D_2O Real-Time Measurement Using Mid-IR Lasers with a Wavelength of 2.9 μm and 3.9 μm

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Liquid phase H_2O and D_2O were measured with mid-IR lasers with wavelengths of 2.9 μm and 3.9 μm. The laser power change over time was observed when the water isotope specie was continuously replaced. Additionally, the concentration ratio of H_2O and D_2O as a function of time was obtained. These results indicate that quantitative measurement of water isotopes using mid-IR lasers in real-time has been successful.

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The geoscience and nuclear fusion fields have investigated the transfer/diffusion of water isotopes such as H_2O, HDO, and HTO [1, 2]. Thus, a real-time measurement method was required to discuss this phenomenon quantitatively and constantly monitor it. Mid-IR laser absorption spectroscopy is an effective method to realize the real-time measurement of water isotopes. H_2O, HDO, and HTO have a strong absorption peak in wavelengths of 3.0 μm, 4.0 μm, and 4.4 μm, which is attributed to the hydroxyl group stretching mode [3, 4]. Therefore, a high-sensitivity absorption measurement of water isotopes can be realized by using a mid-IR light source. Also, laser absorption measurement has the advantage of high time resolution and high sensitivity than measurement by lamp-source due to the laser with higher monochromaticity and brightness. Therefore, we tried to develop a real-time measurement system for water isotopes using mid-IR lasers. In this research, as the first step, we demonstrated the proof-of-principle of liquid-phase H_2O and D_2O measurement using mid-IR lasers.

Figure 1 shows a liquid phase H_2O and D_2O detection system using a mid-IR laser for measuring the time trend of detected laser power passed through a sample cell when changing water isotope species. This system was mainly constructed with lasers, a dichroic mirror (DM) with high transmittance in 3.0 μm and high reflectance in 4.0 μm, a sample cell, a band-pass filter with high transmittance in 4.0 μm, and a power meter. In this system an Er:YAP continuous-wave (CW) laser with a wavelength of 2.9 μm [5] and Quantum a Cascade Laser: QCL (Thorlabs, QF4050C2) with a wavelength of 3.9 μm were used as a beam probe. These lasers entered a sample cell at the same time and an optical path. The sample cell was constructed

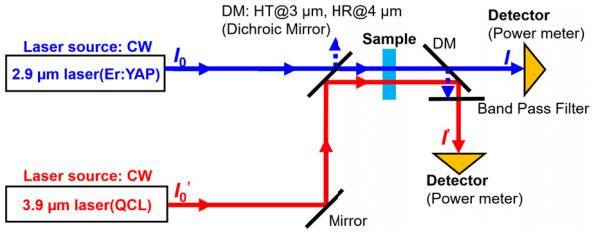

Fig. 1 Experimental setup of laser measurement for water isotopes.

with two sapphire plates of 10 × 10 × 0.3t mm, and the cell length was around 1 μm. The diameter of these incident beams was 5 mm at the cell. After the laser beams passed through the cell, 2.9 μm and 3.9 μm lasers were measured with power meter1 (Thorlabs, S350C) and power meter2 (Thorlabs, S314C) which have a power resolution of 1 mW and response time of 1 s. In this experiment, purified water (H_2O) and heavy water (D_2O) with a concentration of 99.95% (Merck, 1.13366.0009) were used as a sample. Here the D_2O was used as a test sample instead of HDO to observe absorption in 4.0 μm caused by the OD-stretching mode. While the sample cell was irradiated with lasers, the water isotope species of the inside cell was replaced by a capillary force. The sample cell was fixed in space using a clip-stand. The H_2O or D_2O was placed under the cell and attached to the bottom of the cell by a lifting device. After attaching the water to the bottom of the cell, it gradually soaked into the cell by capillary force.

Figure 2 (a) is the detected laser power in a wavelength of 2.9 μm and 3.9 μm as a function of time while changing water isotope species. The time regions of #1, #2, and #3 in Fig. 2 (a) mean that the component inside the cell was replaced air with H_2O, H_2O with D_2O, and D_2O with H_2O, respectively. At 24 s, 351 s, and 772 s, each sample was

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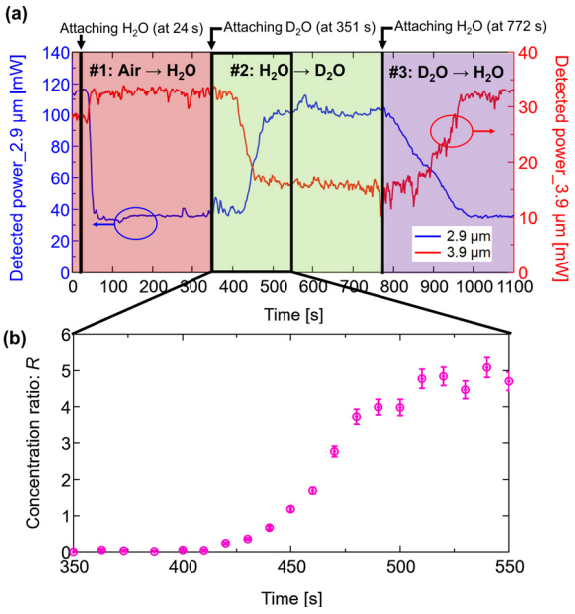

Fig. 2 (a) Detected laser power as a function of time. (b) Concentration ratio from 350 s to 550 s.

attached to the bottom of the cell. From 0 s to 24 s when did not exist water in the cell, averaged laser powers ($I_{\mathrm{in},3}$ and $I_{\mathrm{in},4}$) in 2.9 μm and 3.9 μm were calculated. The values were used as a reference for incident laser power in this experiment. The $I_{\mathrm{in},3}$ and $I_{\mathrm{in},4}$, which were removed Fresnel loss from raw data, were 152.5 mW and 36.8 mW. The rapid increase of 3.9 μm laser power around 40 s was attributed to decreasing reflection loss because the refractive index difference was decreased when the air in the cell was changed to water. In #1, laser power in 2.9 μm dramatically decreased by around 35.5 mW and laser power in 3.9 μm keep a constant value of 32.7 mW. Comparing $I_{\mathrm{in},3}$ to averaged 2.9 μm laser power from 132 s to 164 s, the transmittance of H_2O was 30.9%. This result indicates that the cell was full of H_2O and the 2.9 μm laser was strongly absorbed by it. In #2, laser power in 3.9 μm decreased by 16.1 mW, and that in 2.9 μm increased to around 100 mW. This result suggests that the amount in the cell replaced H_2O with D_2O and the absorption in 3.9 μm by D_2O became dominant. In #3, the laser power in 2.9 μm decreased by 35.5 mW, and that in 3.9 μm increased by 32.3 mW due to the replacement of D_2O with H_2O in the sample cell.

The concentration ratio of D_2O and H_2O ($R = C_{\mathrm{D2O}}/C_{\mathrm{H2O}}$) was derived from the absorbance in 2.9 μm and 3.9 μm defined by detected laser power ($I_{\mathrm{out},3}$ and $I_{\mathrm{out},4}$) and incident laser power. The absorbance A_3 in 2.9 μm or A_4 in 3.9 μm was expressed $A_{\mathrm{i}} = \log 10(I_{\mathrm{in,i}}/I_{\mathrm{out,i}}) = k_{\mathrm{i}}L$, where $k_{\mathrm{i}} = \varepsilon_{\mathrm{H2O_i}}C_{\mathrm{H2O}} + \varepsilon_{\mathrm{D2O_i}}C_{\mathrm{D2O}}$ ($i = 3, 4$). The $\varepsilon_{\mathrm{H2O_3}}/\varepsilon_{\mathrm{H2O_4}}$ and $\varepsilon_{\mathrm{D2O_3}}/\varepsilon_{\mathrm{D2O_4}}$ were the molar extinction coefficient of H_2O in 3.0 μm/4.0 μm and D_2O in 3.0 μm/4.0 μm region, and these were summarized in Table 1. L was a sample length. The $\varepsilon_{\mathrm{H2O_3um}}$ and $\varepsilon_{\mathrm{H2O_4um}}$ were estimated from an absorption coefficient (α) in 2.9 μm or 3.9 μm of H_2O [6] and the Lambert-Beer Law of $I_{\mathrm{out}} = I_{\mathrm{in}}10^{(-\varepsilon CL)} = I_{\mathrm{in}}\exp(-\alpha L)$. Finally, the concentration ratio R(t) was expressed by transforming the ratio of absorbance (A_3/A_4) as shown in (1).

Table 1 Molar extinction coefficient of H2O in 3.0 μm, D2O in 3.0 μm, H2O in 4.0 μm, and D2O in 4.0 μm region [6,7].

	$\varepsilon_{\mathrm{H2O_3}}$	$\varepsilon_{\mathrm{D2O_3}}$	$\varepsilon_{\mathrm{H2O_4}}$	$\varepsilon_{\mathrm{D2O_4}}$
[L/(mol·cm)]	152.5	43.6	45.4	123.0

$$\frac{C_{\mathrm{D2O}}}{C_{\mathrm{H2O}}} = \frac{A_3\varepsilon_{\mathrm{H2O_4}} - A_4\varepsilon_{\mathrm{D2O_3}}}{A_4\varepsilon_{\mathrm{D2O_3}} - A_3\varepsilon_{\mathrm{D2O_4}}} = R(t). \quad (1)$$

Figure 2 (b) shows R(t) from 350 s to 550 s while replacing H_2O with D_2O. Around 351 s, the R was almost zero. This result suggests that the D_2O was not in the cell in the time region. Around 420 s, an increase in R(t) was observed because the D_2O gradually soaked into the cell. Finally, the R(t) was increased until around 500 s, and the value was saturated at around 5.0 in 550 s. This result indicates that the replacement of H_2O with D_2O reached an equilibrium. Although D_2O was completely replaced with H_2O after 1000 s in #3, in #2, H_2O existed in the sample cell because part of D_2O in the cell was replaced by H_2O in the atmosphere. From these results, we have succeeded in quantitative observation of the dynamics of an H_2O and D_2O transfer phenomenon using mid-IR lasers.

In summary, H_2O and D_2O in a liquid phase were measured with 2.9 μm and 3.9 μm lasers when a component of water isotope species inside a cell was continuously changed. Also, a concentration ratio as a function of time was obtained from laser measurement. Thus, we succeeded in quantitative measurement of a water isotope using a mid-IR laser in real-time.

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