

# Preliminary Results of H<sub>2</sub>O and D<sub>2</sub>O Real-Time Measurement Using Mid-IR Lasers with a Wavelength of 2.9 $\mu$ m and 3.9 $\mu$ m

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(Received 6 January 2022 / Accepted 1 April 2022)

Liquid phase H<sub>2</sub>O and D<sub>2</sub>O were measured with mid-IR lasers with wavelengths of 2.9  $\mu$ m and 3.9  $\mu$ m. The laser power change over time was observed when the water isotope specie was continuously replaced. Additionally, the concentration ratio of H<sub>2</sub>O and D<sub>2</sub>O 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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Keywords: water isotope, mid-IR laser, laser absorption measurement

DOI: 10.1585/pfr.17.1205057

The geoscience and nuclear fusion fields have investigated the transfer/diffusion of water isotopes such as H<sub>2</sub>O, 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<sub>2</sub>O, HDO, and HTO have a strong absorption peak in wavelengths of 3.0  $\mu$ m, 4.0  $\mu$ m, and 4.4  $\mu$ m, 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<sub>2</sub>O and D<sub>2</sub>O measurement using mid-IR lasers.

Figure 1 shows a liquid phase H<sub>2</sub>O and D<sub>2</sub>O 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  $\mu$ m and high reflectance in 4.0  $\mu$ m, a sample cell, a band-pass filter with high transmittance in 4.0  $\mu$ m, and a power meter. In this system an Er:YAP continuous-wave (CW) laser with a wavelength of 2.9  $\mu$ m [5] and Quantum a Cascade Laser: QCL (Thorlabs, QF4050C2) with a wavelength of 3.9  $\mu$ m 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

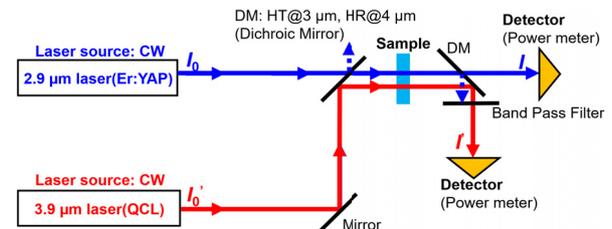


Fig. 1 Experimental setup of laser measurement for water isotopes.

with two sapphire plates of 10 × 10 × 0.3t mm, and the cell length was around 1  $\mu$ m. The diameter of these incident beams was 5 mm at the cell. After the laser beams passed through the cell, 2.9  $\mu$ m and 3.9  $\mu$ m 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<sub>2</sub>O) and heavy water (D<sub>2</sub>O) with a concentration of 99.95% (Merck, 1.13366.0009) were used as a sample. Here the D<sub>2</sub>O was used as a test sample instead of HDO to observe absorption in 4.0  $\mu$ m 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<sub>2</sub>O or D<sub>2</sub>O 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  $\mu$ m and 3.9  $\mu$ m 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<sub>2</sub>O, H<sub>2</sub>O with D<sub>2</sub>O, and D<sub>2</sub>O with H<sub>2</sub>O, respectively. At 24 s, 351 s, and 772 s, each sample was

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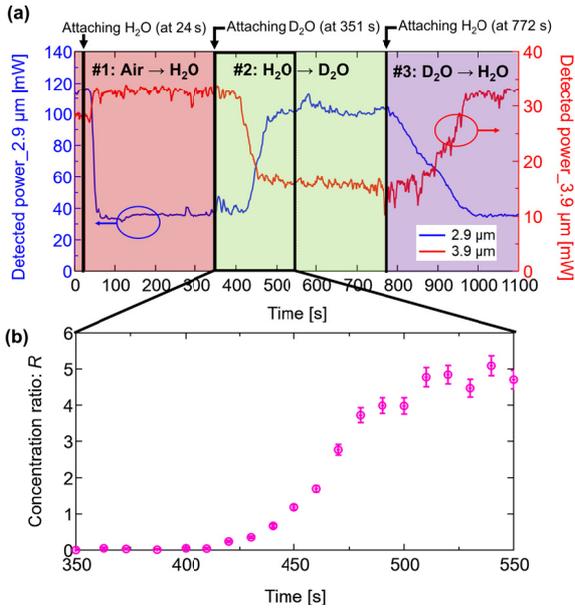


Fig. 2 (a) Detected laser power as a function of time. (b) Concentration ratio from 350 s to 550 s.

attached to the bottom of the cell. From 0 s to 24 s when did not exist water in the cell, averaged laser powers ( $I_{in,3}$  and  $I_{in,4}$ ) in 2.9  $\mu\text{m}$  and 3.9  $\mu\text{m}$  were calculated. The values were used as a reference for incident laser power in this experiment. The  $I_{in,3}$  and  $I_{in,4}$ , which were removed Fresnel loss from raw data, were 152.5 mW and 36.8 mW. The rapid increase of 3.9  $\mu\text{m}$  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  $\mu\text{m}$  dramatically decreased by around 35.5 mW and laser power in 3.9  $\mu\text{m}$  keep a constant value of 32.7 mW. Comparing  $I_{in,3}$  to averaged 2.9  $\mu\text{m}$  laser power from 132 s to 164 s, the transmittance of H<sub>2</sub>O was 30.9%. This result indicates that the cell was full of H<sub>2</sub>O and the 2.9  $\mu\text{m}$  laser was strongly absorbed by it. In #2, laser power in 3.9  $\mu\text{m}$  decreased by 16.1 mW, and that in 2.9  $\mu\text{m}$  increased to around 100 mW. This result suggests that the amount in the cell replaced H<sub>2</sub>O with D<sub>2</sub>O and the absorption in 3.9  $\mu\text{m}$  by D<sub>2</sub>O became dominant. In #3, the laser power in 2.9  $\mu\text{m}$  decreased by 35.5 mW, and that in 3.9  $\mu\text{m}$  increased by 32.3 mW due to the replacement of D<sub>2</sub>O with H<sub>2</sub>O in the sample cell.

The concentration ratio of D<sub>2</sub>O and H<sub>2</sub>O ( $R = C_{D2O}/C_{H2O}$ ) was derived from the absorbance in 2.9  $\mu\text{m}$  and 3.9  $\mu\text{m}$  defined by detected laser power ( $I_{out,3}$  and  $I_{out,4}$ ) and incident laser power. The absorbance  $A_3$  in 2.9  $\mu\text{m}$  or  $A_4$  in 3.9  $\mu\text{m}$  was expressed  $A_i = \log_{10}(I_{in,i}/I_{out,i}) = k_i L$ , where  $k_i = \epsilon_{H2O,i} C_{H2O} + \epsilon_{D2O,i} C_{D2O}$  ( $i = 3, 4$ ). The  $\epsilon_{H2O,3}/\epsilon_{H2O,4}$  and  $\epsilon_{D2O,3}/\epsilon_{D2O,4}$  were the molar ex-

Table 1 Molar extinction coefficient of H<sub>2</sub>O in 3.0  $\mu\text{m}$ , D<sub>2</sub>O in 3.0  $\mu\text{m}$ , H<sub>2</sub>O in 4.0  $\mu\text{m}$ , and D<sub>2</sub>O in 4.0  $\mu\text{m}$  region [6, 7].

	$\epsilon_{H2O,3}$	$\epsilon_{D2O,3}$	$\epsilon_{H2O,4}$	$\epsilon_{D2O,4}$
[L/(mol·cm)]	152.5	43.6	45.4	123.0

inction coefficient of H<sub>2</sub>O in 3.0  $\mu\text{m}$ /4.0  $\mu\text{m}$  and D<sub>2</sub>O in 3.0  $\mu\text{m}$ /4.0  $\mu\text{m}$  region, and these were summarized in Table 1.  $L$  was a sample length. The  $\epsilon_{H2O,3\mu\text{m}}$  and  $\epsilon_{H2O,4\mu\text{m}}$  were estimated from an absorption coefficient ( $\alpha$ ) in 2.9  $\mu\text{m}$  or 3.9  $\mu\text{m}$  of H<sub>2</sub>O [6] and the Lambert-Beer Law of  $I_{out} = I_{in}10^{(-\epsilon CL)} = I_{in} \exp(-\alpha L)$ . Finally, the concentration ratio  $R(t)$  was expressed by transforming the ratio of absorbance ( $A_3/A_4$ ) as shown in (1).

$$\frac{C_{D2O}}{C_{H2O}} = \frac{A_3 \epsilon_{H2O,4} - A_4 \epsilon_{D2O,3}}{A_4 \epsilon_{D2O,3} - A_3 \epsilon_{D2O,4}} = R(t). \quad (1)$$

Figure 2 (b) shows  $R(t)$  from 350 s to 550 s while replacing H<sub>2</sub>O with D<sub>2</sub>O. Around 351 s, the  $R$  was almost zero. This result suggests that the D<sub>2</sub>O was not in the cell in the time region. Around 420 s, an increase in  $R(t)$  was observed because the D<sub>2</sub>O 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<sub>2</sub>O with D<sub>2</sub>O reached an equilibrium. Although D<sub>2</sub>O was completely replaced with H<sub>2</sub>O after 1000 s in #3, in #2, H<sub>2</sub>O existed in the sample cell because part of D<sub>2</sub>O in the cell was replaced by H<sub>2</sub>O in the atmosphere. From these results, we have succeeded in quantitative observation of the dynamics of an H<sub>2</sub>O and D<sub>2</sub>O transfer phenomenon using mid-IR lasers.

In summary, H<sub>2</sub>O and D<sub>2</sub>O in a liquid phase were measured with 2.9  $\mu\text{m}$  and 3.9  $\mu\text{m}$  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.

This work was supported by JAPS KAKENHI Grant Number (20J15317).

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