Isotope analysis of water by means of near-infrared dual-wavelength diode laser spectroscopy

L. Gianfrani*, G. Gagliardi*, M. van Burgel, and E. R. Th. Kerstel
Centrum voor IsotopenOnderzoek, University of Groningen
Nijenborgh 4, Groningen, 9747AG, The Netherlands
kerstel@phys.rug.nl

* Permanent address: Dipartimento di Scienze Ambientali, Seconda Università di Napoli, and
INFM – Gruppo Coordinato Napoli 2,
Via Vivaldi 43, I-81100 Caserta, Italy

Abstract: A novel diode laser spectrometer was developed using dual-wavelength multiplexing, ensuring ideal conditions for high-precision and simultaneous measurements of the $\text{^2H/}^{1}\text{H}$, $\text{^{17O/}^{16O}}$, and $\text{^{18O/}^{16O}}$ isotope ratios in water. A 1.4-µm diode laser probed a $\text{H}^{16}\text{OH} / \text{HO}^{18}\text{O}$ line pair near 7198 cm$^{-1}$, while a similar laser observed $\text{H}^{16}\text{OH}$, $\text{H}^{17}\text{OH}$, and $\text{H}^{18}\text{OH}$ ro-vibrational lines around 7183 cm$^{-1}$, or a $\text{H}^{16}\text{OH} / \text{H}^{18}\text{OH}$ line pair near 7200 cm$^{-1}$. The 1-$\sigma$ standard deviation is 0.2‰ for $\text{^{18O/}^{16O}}$, and 0.5‰ for the $\text{^2H/}^{1}\text{H}$ and $\text{^{17O/}^{16O}}$ isotope ratios. Preliminary experiments with repeated injections of a natural abundance sample point to an accuracy of about 1‰ for all three isotope ratios in natural samples.

©2003 Optical Society of America

OCIS codes: (300.1030) Spectroscopy: Absorption; (300.6190) Spectroscopy: Spectrometers; (300.6260) Spectroscopy: Spectroscopy, diode lasers

References and links


1. Introduction

Optical techniques for stable isotope analysis have attracted a growing interest in recent years, because of the need of valid alternatives to isotope ratio mass spectrometry (IRMS) [1]. In fact, although commercially available with a potentially very high precision and throughput, IRMS instrumentation is expensive, bulky, and usually requires a skilled technician for its operation. IRMS is also not compatible with condensable gases, such as water, which require chemical conversion of the sample to more easily analyzed gases. These chemical preparatory steps limit the overall throughput and often also the final precision and accuracy. In addition, they complicate the on-line, continuous analysis of samples. Water is certainly one of the unluckiest cases. Reduction of water to H\textsubscript{2} or equilibration with CO\textsubscript{2} is necessary in order to determine 2H and 18O isotope ratios, respectively. Isotope ratio measurements of 17O are virtually impossible, as the 17OCO and 13CO\textsubscript{2} molecules appear in the same mass channel.

On the other hand, diode laser spectroscopy has been widely recognized as a powerful tool for trace-gas diagnostics, fast and accurate concentration measurements being possible in a large variety of environments [2-4]. Very interesting advances have been made in the field of multiple-gas sensing. The use of multiple independently operated diode lasers in conjunction with optical fiber components has enabled the development of multiple-gas analyzers capable of measuring temperature, pressure and concentrations in a single optical path configuration [5]. Compact and robust systems have been implemented for field measurements, often in hostile conditions like those of a volcanic site [6]. Multiple-gas sensing can be performed using different approaches. In the multiplexed configuration, one laser can be activated at a time providing a sequential operation at a given repetition frequency [7,8]. Recently, continuous and simultaneous probing of different species in a two-laser set-up has been reported, using an original scheme based on wavelength modulation spectroscopy [9]. In this case, the two lasers were modulated at incommensurate frequencies and detected by the same photodiode, whose amplitude-modulated output signal was processed by two different lock-in amplifiers. In this paper, we demonstrate that a similar spectroscopic design can be successfully applied to the precise and simultaneous determination of the H\textsubscript{2}/H, 17O/16O, and 18O/16O isotope abundance ratios in water. This is not an obvious issue, as the precision requirements of isotope ratio measurements are such that cross-talk between the two wavelength channels may not exceed about 1 in 10\textsuperscript{4}. In particular for tunable diode laser isotope ratio measurements, wavelength multiplexing provides a major advantage, as most such experiments are severely hampered by the requirement of finding all isotopomers of interest absorbing within the limited tuning range of the laser, at near equal intensities, and without interfering spectral overlap or unfavorable temperature dependencies.

At the Groningen Center for Isotope Research, we have already shown the capability of infrared laser spectroscopy to measure isotope ratios in small water samples in the gas phase, exciting the fundamental OH-stretching vibration at 2.7 \mu m [10]. The isotope ratios were determined from simultaneously recorded, direct absorption spectra in parallel sample and reference gas cells, the latter being filled with a local reference material, back-traceable to international standards such as Standard Light Antarctic Precipitation (SLAP) and Vienna Standard Mean Ocean Water (VSMOW). The instrument used a commercial color center laser as its infrared light source. The accuracy for routine measurements was of the order of 0.5‰ for the oxygen isotope ratios and of about 1‰ for the deuterium isotope ratio for natural
samples, sufficient for successful application of the instrument to studies in paleoclimatology [11] and biomedicine [12]. More recently, we have also shown that a distributed feedback diode laser, operating near 1.39 µm, can replace the color center laser with a large number of technical advantages, including a higher spectral purity, lower frequency and amplitude noise, and much better performance in terms of frequency control and modulation, in addition to the practical advantages of low cost, small size and weight, and low power consumption. In spite of the relatively small line intensities associated with the overtone or combination vibrations at 1.4 µm, promising results were obtained for the \(^2\)H/\(^1\)H, \(^{17}\)O/\(^{16}\)O, and \(^{18}\)O/\(^{16}\)O isotope ratios using wavelength modulation spectroscopy [13]. As in the case of the color center laser set-up, the simultaneous measurements of these three ratios was possible thanks to the fortuitous occurrence of suitable ro-vibrational lines of the \(^{18}\)OH, \(^{17}\)OH, \(^{18}\)OH, and \(^{18}\)O\(^2\)H isotopomers within a single laser frequency scan of about 1 cm\(^{-1}\) wide. These operating conditions (corresponding to an injection current variation of 40 mA), in which the diode laser current periodically approaches the threshold and maximum values, are particularly ill-suited for \(^2\)H/\(^1\)H determinations, as the \(^{18}\)O\(^2\)H line occurred at the lower end of the current scan. As a consequence, the signal-to-noise ratio on the \(^{18}\)O\(^2\)H line was not sufficiently high to reach the high level of precision required in most applications.

Here, we report on a dual-wavelength spectrometer, ensuring ideal conditions for high-precision and simultaneous analysis of \(^2\)H/\(^1\)H, \(^{17}\)O/\(^{16}\)O, and \(^{18}\)O/\(^{16}\)O in water. This scheme, operating with a pair of 1.4-µm diode lasers, provides the opportunity to select the most advantageous line pairs considering line intensities and their temperature dependencies. Without the requirement of finding all isotopomers of interest (the most abundant \(^{16}\)OH and the rare \(^{18}\)O\(^2\)H, \(^{18}\)OH, and \(^{18}\)OH) absorbing in the same small spectral range, but with two such spectral regions available, it is considerably easier to find transitions of all four isotopomers, suitable in terms of intensities, spectral overlap, and temperature dependencies. Thus, in this case, one laser was tuned to probe a \(^{18}\)OH / \(^{18}\)O\(^2\)H line pair near 7198 cm\(^{-1}\), while a second laser was scanned over \(^{18}\)OH, \(^{18}\)OH, and \(^{18}\)OH lines around 7183 cm\(^{-1}\) (or a \(^{18}\)OH / \(^{18}\)OH line pair near 7200 cm\(^{-1}\) ), to measure all three isotope ratios (or just the two most frequently desired) with a precision of better than 1‰.

2. Experimental setup

Figure 1 shows the experimental setup, consisting of the diode laser system, two multiple-reflection cells and the detection system.
Fig. 1. Sketch of the experimental setup. OI stands for optical isolator, LIA for lock-in amplifier, and DL for diode laser.

The diode lasers are of the InGaAsP/InP type, with a distributed feedback (DFB) structure and were bought individually at different times from Sensors Unlimited. Their specifications differ significantly, most prominently in beam quality and output power. The first (DL1) emits about 1 mW in a single mode around 1.392 µm, while the second laser (DL2) can deliver up to 10 mW at a wavelength of 1.389 µm. Both lasers operate at or near room temperature. Home-built current generators and (thermo-electric) temperature controllers were used to drive the diode laser sources. In the wavelength multiplexed experiments DL1 was wavelength tuned over vib-rotational lines of H16OH, H17OH, and H18OH isotopomers, with a periodic modulation of the injection current providing a 0.5 cm⁻¹ wide scan at a repetition rate of 0.125 Hz. At the same time, DL2 was tuned into coincidence with H16OH and HO2H lines by means of a frequency scan as large as 0.6 cm⁻¹, which was performed at the same repetition rate and in phase with that of DL1. For this purpose, a single triangular wave was used with an individually adjustable gain on each modulation channel.

The two laser beams were combined through a pair of half-wave plates and a polarizing cube, thus producing a two-color beam with crossed polarization components. This beam was split into two parts of equal intensities, which were subsequently sent to the two gas cells. The optical path-length inside the multiple-pass cells was 20.5 m in a 48-pass configuration. The use of a pair of cells enables one to measure the isotope ratio in a sample gas with respect to that of a reference gas and, hence, to determine the δ-values in a manner as described previously [10]. A vacuum system, based on an oil-free molecular-drag pump, ensured high purity in the gas cells. The liquid water samples were injected into the gas cell through a silicon membrane using a 10 µl syringe. Simultaneous operation of the two lasers was possible using frequency modulation multiplexing. The diode lasers were modulated at incommensurate frequencies of approximately 18 and 27 kHz. The modulation frequencies were chosen with particular care in order to optimize the signal-to-noise ratio and to avoid potential cross-talk effects among the absorption signals at the two wavelengths. This was accomplished using a Fourier transform spectrum analyzer, which enabled us to compare the amplitude noise spectra in the range 0-100 kHz associated with the transmission of one of the gas cells with one laser activated at a time and, subsequently, with both lasers operating simultaneously. A Ge photodetector was used to monitor the transmitted power for each cell. Two pairs of lock-in amplifiers were used to process the signals carrying information on the
absorption phenomena occurring in the two gas cells. Particularly, a pair of digital lock-in amplifiers (Stanford for Research SR830) monitored the signals corresponding to DL$_2$, while two analog lock-in amplifiers (EG&G 5210) were dedicated to those coming from DL$_1$.

Wavelength modulation spectroscopy with first harmonic (1-$f$) detection was implemented with the modulation index set to about 2. First-harmonic detection was selected over second-harmonic detection, based on preliminary experiments. It was concluded that the reduced amplitude modulation in a 2-$f$ scheme does not compensate for the loss of signal strength. The lock-in time constants were equal to 10 ms with digital filtering of 24 dB/oct for the digital lock-ins, and 30 ms with 6 dB/oct, for the analog models. Signal averaging over 10 scans was performed to further reduce the equivalent noise detection bandwidth (ENDB) down to about 1 Hz in each case.

As shown schematically in Fig. 1, the digital lock-in amplifiers were interfaced to a personal computer through a GPIB interface, while auxiliary analog-to-digital converters of the digital lock-ins were used to acquire the output signals of the analog lock-in amplifiers with 16-bit resolution. In this way, four data vectors (2048-record length) were initially stored in the buffers of the two digital lock-in amplifiers before being transferred to the personal computer, thus enabling the fully automated acquisition of spectra for many hours without operator intervention.

The alignment of the multiple-reflection cells was performed with utmost care in order to minimize interference effects, which could introduce spurious amplitude modulated signals, thus disturbing the absorption signals. No periodic modulation of the baseline, due to “fringes”, was observable in the present setup. In addition, great care was taken to insure mechanical and thermal stability. Particularly, the entire spectrometer was enclosed in a sealed plexi-glas box, which was shown to be already quite effective in reducing thermal variations between the gas cells. A second box of thermally insulating foam provided further passive thermal stabilization of the gas cells. This is a crucial point, as a temperature difference of 1 °C between the sample and reference cells may easily introduce a systematic error in the relative isotope ratio values of the order of 1‰, depending on the temperature coefficients of the ro-vibrational lines. The temperature coefficient is defined as the relative variation of the line strength corresponding to a temperature increase of 1 K at 296 K, and may be expressed in ºC/k. Table 1 gives the temperature coefficients of the ro-vibrational transitions used in this study, together with their ro-vibrational assignments based on the spectroscopic data reported by R. A. Toth [14-16]. The temperature coefficients were calculated from the ground state energies $E''$ using the following formula for the temperature dependence of the line strength $S$ at constant volume:

$$S(T) = S(T_0) \left( \frac{T}{T_0} \right)^{3/2} \exp \left[ -\frac{he}{k} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right].$$

This formula neglects the effects of stimulated emission (a very good approximation in the infrared), and was derived assuming a classical expression for the rotational partition function, while ignoring the temperature dependence of the vibrational partition function (see, e.g., formulas 5 and 6 in Ref. [1]).

The temperature sensitivity of the isotope ratio measurement ($\delta$-value; see below) is in very good approximation equal to the difference in temperature coefficients of the ro-vibrational transitions involved (i.e., of rare and abundant isotopomer).
Table 1. List of the absorption lines observed in this work. Line positions and assignments were taken from Refs. [14-16]. The temperature coefficients were evaluated at 296 K.

<table>
<thead>
<tr>
<th>Isotopomer</th>
<th>Position (cm⁻¹)</th>
<th>Vibrational band</th>
<th>Rotational assignment</th>
<th>Ground state energy [cm⁻¹]</th>
<th>Temperature coefficient (‰/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H¹⁸OH</td>
<td>7183.5871</td>
<td>ν₁ + ν₃</td>
<td>5₀₉→₅₁₀</td>
<td>733.7</td>
<td>+6.9</td>
</tr>
<tr>
<td>H¹⁶OH</td>
<td>7183.6858</td>
<td>2ν₃</td>
<td>6₃₃→₅₂₄</td>
<td>661.6</td>
<td>+5.7</td>
</tr>
<tr>
<td>H¹⁷OH</td>
<td>7183.7356</td>
<td>ν₁ + ν₃</td>
<td>2¹₁→₁₀</td>
<td>94.8</td>
<td>-3.4</td>
</tr>
<tr>
<td>H¹⁶OH</td>
<td>7197.5505</td>
<td>2ν₁</td>
<td>6₂₄→₇₁₄</td>
<td>586.5</td>
<td>+4.4</td>
</tr>
<tr>
<td>HO₂H</td>
<td>7197.9507</td>
<td>2ν₁</td>
<td>3₁₂→₂₂₁</td>
<td>116.5</td>
<td>-3.1</td>
</tr>
<tr>
<td>H¹⁸OH</td>
<td>7199.9608</td>
<td>ν₁ + ν₃</td>
<td>5₃₂→₅₃₃</td>
<td>505.7</td>
<td>+3.1</td>
</tr>
<tr>
<td>H¹⁶OH</td>
<td>7200.1338</td>
<td>2ν₁</td>
<td>4₂₂→₅₁₅</td>
<td>315.8</td>
<td>+0.03</td>
</tr>
</tbody>
</table>

3. Results and discussion

An example of acquired spectra is shown in Fig. 2.

![Spectra example](image)

Fig. 2. Examples of absorption spectra observed in this work in two different spectral windows. The first includes H¹⁸OH, H¹⁶OH, and H¹⁷OH lines around 7183.7 cm⁻¹, while the second shows HO₂H and H¹⁶OH lines at 7197.95 and 7197.55 cm⁻¹, respectively.

We may note the excellent signal-to-noise ratio, which was measured to be about 10⁴ for the H¹⁶OH line at 7197.5505 cm⁻¹ and 3 × 10³ for the H¹⁸OH line at 7183.5871 cm⁻¹, with an ENBW of 1.2 Hz and 0.8 Hz, respectively.

Using the so-called δ-notation, the isotopic composition of a sample with respect to that of a reference material is given by, for instance in the case of ¹⁸O in water:

\[
\delta^{18}O = \frac{\left(\frac{n_{18}}{n_{16}}\right)_{sample}}{\left(\frac{n_{18}}{n_{16}}\right)_{reference}} - 1 = \frac{\left(\frac{n_{18}}{n_{16}}\right)_{sample}}{\left(\frac{n_{18}}{n_{16}}\right)_{reference}} - 1, \tag{2}
\]

\(n_{18}\) and \(n_{16}\) being the H¹⁸OH and H¹⁶OH number densities. Since the δ-value is generally very small, it is usually expressed as per mil (‰). The usual international standard reference...
material for water is VSMOW, although in practice a local reference material is used as the working standard, which is well-known with respect to VSMOW. The water vapor pressure was about 10 Torr, which lead to a maximum fractional absorption at line center of less than 5% for the strongest lines, due to H\textsuperscript{18}OH and H\textsuperscript{16}OH. At this value of absorption, the deviation from linearity of the Lambert-Beer law is about 2.6%. Since for all practical purposes the abundance of H\textsuperscript{16}OH does not change, we need only worry about underestimating the absorption of the rare isotopomer. However, only at relatively large isotopic abundance differences between sample and reference material, will this lead to a sizable error in the determined isotope δ-value of Eq. (2). For example, if one measures a sample with δ\textsuperscript{18}O = -50‰ (this would be about the most depleted natural water to be found on Earth on Antarctica), the systematic error on this account would be about 1.3‰. In our case of samples of identical or very similar isotopic composition, the maximum absorption of 5% is sufficiently low to ensure that we may safely ignore the effect of Lambert-Beer non-linearity. The δ-values are retrieved by means of a line-by-line non-linear least squares fit of the sample spectrum to the sum of the reference spectrum and a linear or quadratic baseline, multiplied by a factor representing the ratio of the isotopomer concentrations, in a manner as described in Ref. [10]. This procedure requires a careful determination of the line centers and is performed, for each isotopomer, over a frequency range as wide as 3 times the full-width-at-half-maximum, symmetric with respect to the line center.

The analytical capabilities of the dual-wavelength spectrometer were carefully tested and optimized through a large number of measurements performed with initially one laser activated at a time and, subsequently, with both lasers operating simultaneously. For this purpose, both gas cells were filled with 10 µl of identical de-mineralized water. We thus expect to measure a δ-value of zero. The most interesting performances were obtained with the δ\textsuperscript{2}H determination, using DL\textsuperscript{2}. In Fig. 3, the results of precision tests, over short (upper part) and long (lower part) time spans, are shown.

As each measurement took 160 s, the total acquisition times were equal to 80 and 400 minutes for series of 30 and 150 measurements. Of these, measurements that were removed more than 3.5 times the absolute deviation from the median were excluded from the figure and further statistical analysis. In this way, in a typical experiment between 5% and 10% of the measurements were considered to be outliers. For the measurements of Fig. 3 we found a 1-σ precision of 0.5‰ and 0.8‰ for the 80 and 400 minute time-span series, respectively. It is interesting to note that the δ-values appear to change periodically between −0.5‰ and +2.5‰. This may be attributed to a small temperature difference between the two cells, the temperature coefficients of the HO\textsuperscript{2}H and H\textsuperscript{18}OH lines indicating a drift of about 0.5 K.
Fig. 3. Short and long term reproducibility in the δ²H determination, using DL₂.
The statistical analysis of the values reported in the upper plot yielded a mean value of 1.08‰ and a 1-σ standard deviation of 0.46‰. For the values in the lower part of the figure, we found a mean value of 1.09‰ and a standard deviation of 0.84‰. "Label" refers to a single measurement of 160 s.

We also checked the reproducibility over several days through different series of measurements, each time filling both cells with 10 µl of the same de-mineralized water, followed by evacuation, flushing, and refilling, before starting a new series. Over a time interval of six days, we found mean values ranging from –0.73‰ to +1.68‰, with an overall average value of 0.48‰ and a standard deviation (1-σ) of 1‰. This test also provides preliminary information on the level of accuracy. Through the measurement of two or more reference materials of well-known isotopic composition, the reproducibility may be transferred into a measurement accuracy over the range spanned by the reference materials. Although a non-zero average δ-value indicates the presence of a systematic deviation, the average δ²H-value was well within the long-term precision level. The results of the long-term reproducibility test are presented in Table 2.

Table 2. Examples of δ²H determinations at 7198 cm⁻¹ by means of DL₂. Set dimension is the number of remaining measurements after removal of outliers from the original 20 or 30 measurements (see text).

<table>
<thead>
<tr>
<th>Date</th>
<th>Set dimension</th>
<th>Mean value (‰)</th>
<th>Standard deviation (‰)</th>
<th>Standard error (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sept 19, 2002</td>
<td>25</td>
<td>1.60</td>
<td>0.80</td>
<td>0.16</td>
</tr>
<tr>
<td>Sept 19, 2002</td>
<td>19</td>
<td>0.26</td>
<td>1.00</td>
<td>0.23</td>
</tr>
<tr>
<td>Sept 21, 2002</td>
<td>27</td>
<td>-0.73</td>
<td>0.74</td>
<td>0.14</td>
</tr>
<tr>
<td>Sept 21, 2002</td>
<td>27</td>
<td>-0.03</td>
<td>0.87</td>
<td>0.17</td>
</tr>
<tr>
<td>Sept 25, 2002</td>
<td>26</td>
<td>1.05</td>
<td>0.60</td>
<td>0.12</td>
</tr>
<tr>
<td>Sept 26, 2002</td>
<td>27</td>
<td>1.23</td>
<td>0.78</td>
<td>0.15</td>
</tr>
<tr>
<td>Sept 26, 2002</td>
<td>29</td>
<td>1.68</td>
<td>0.84</td>
<td>0.16</td>
</tr>
<tr>
<td>Sept 26, 2002</td>
<td>18</td>
<td>-0.35</td>
<td>0.70</td>
<td>0.16</td>
</tr>
</tbody>
</table>
Table 3. Examples of $\delta^{18}O$ and $\delta^{17}O$ determinations at 7183 cm$^{-1}$, by means of DL$_1$.

<table>
<thead>
<tr>
<th>Date</th>
<th>Set dimension</th>
<th>Mean $\delta^{18}O$ value (‰)</th>
<th>$\delta^{18}O$ standard deviation (‰)</th>
<th>Mean $\delta^{17}O$ value (‰)</th>
<th>$\delta^{17}O$ standard deviation (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sept 23, 2002</td>
<td>30</td>
<td>3.2</td>
<td>0.7</td>
<td>-1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Sept 24, 2002</td>
<td>30</td>
<td>-2.4</td>
<td>0.6</td>
<td>4.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Sept 24, 2002</td>
<td>30</td>
<td>-3.4</td>
<td>1.1</td>
<td>3.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Sept 24, 2002</td>
<td>30</td>
<td>-2.3</td>
<td>0.7</td>
<td>2.8</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Similar tests were performed for the detection of H$^{16}$OH, H$^{17}$OH, and H$^{18}$OH isotopomers by means of DL$_1$. Recording several series of 30 spectra we found values of the short-term reproducibility in the range 0.6‰ to 1.1‰ and 1.4‰ to 1.8‰, for the $\delta^{18}O$ and $\delta^{17}O$ determinations, respectively. Hence, in spite of the much lower available power with respect to DL$_2$, we were able to obtain only slightly inferior results in terms of short-term precision. Nonetheless, the major problem with $\delta^{15}O$ and $\delta^{18}O$ measurements was related to the accuracy, as systematic errors emerged in each series. In Table 3, we report the results of $\delta^{17}O$ and $\delta^{18}O$ determinations in different sets of measurements performed over two days, each time using a new sample of de-mineralized water. We may note different apparent $\delta$-shifts, with the $\delta^{15}O$- and $\delta^{18}O$-values always exhibiting opposite signs. This point deserves a more detailed discussion. We believe that these apparent $\delta$-shifts are due to residual temperature and pressure differences between the two cells, as well as to the partial overlapping of the H$^{16}$OH and H$^{17}$OH lines at 7183 cm$^{-1}$. Particularly, using the temperature coefficients reported in Table 1, we may calculate shifts in the $\delta^{17}O$ and $\delta^{18}O$ values of about +9 and −1‰/K, due to the differential temperature effect alone. In other words, the observed fluctuations in the $\delta^{17}O$ value would suggest a temperature difference between the two cells of 0.7 K. But this temperature difference should lead to much smaller variations in the $\delta^{18}O$-value than those observed experimentally, and reported in Table 3. However, the spectral overlapping of the H$^{16}$OH and H$^{17}$OH lines, clearly visible in Fig. 2, may enhance the effect of a differential temperature on the $\delta^{18}O$-value because of the opposite sign of the H$^{16}$OH and H$^{17}$OH temperature coefficients. Indeed, as a consequence of the partial line overlapping, the effective temperature coefficient for the H$^{18}$OH signal would be lower than that given in Table 1, thus increasing the temperature dependence of the $\delta^{18}O$-value.

Furthermore, a differential pressure may limit the accuracy in the fit of the sample spectrum to the reference one, for each isotopomer individually, because of the different line shapes and widths. Line overlapping may be responsible for pressure-dependent asymmetries in the 1-f profiles, further limiting the accuracy in the spectra analysis. It should be noted that these effects are a direct consequence of the data analysis procedure used, in which a section around each spectral feature in the sample spectrum is fit to the same region in the reference spectrum (with the isotopomer ratio as a multiplicative free parameter). An analysis procedure based on the simultaneous fit of multiple (frequency modulated) absorption profiles to all spectral features present in the recorded spectrum would not suffer from such a differential pressure (line width and line shape) effect. This is because in this case the absorption intensities may be calculated from the line height and line width parameters of the individual line profiles. In the calculation of the $\delta$-value according to Eq. (2), the pressure induced line shape change of the spectral feature corresponding to the rare isotopomer would then be canceled by the same change in the abundant isotopomer line shape. A disadvantage of a simultaneous fit to all spectral features present in the recorded spectrum is the requirement of a proper calibration of the frequency scale. We have observed and extensively studied the above mentioned effects with our color center laser spectrometer at 2.7 µm [10]. We concluded that in most cases the, line-by-line, sample to reference fitting procedure is superior to the multiple line (Voigt) profile procedure, provided that well-calibrated (thus reproducible) corrections are made for the differential pressure between the sample and reference gas cells.
as measured by the line-widths). In fact, we were even able to reproduce the experimentally determined correction factors in a simulation of the data analysis procedure with synthetic spectra. These aspects of the present apparatus are currently being studied in more detail.

The analytical performance of our spectrometer was also tested with both lasers operating simultaneously in the wavelength multiplexed mode. We found the simultaneous operation to be effective, as the precision and reproducibility (upon repeated injection of a fresh sample) levels achieved with each laser separately were not measurably affected by the presence of the other laser.

We also used the better, more powerful diode laser DL2, instead of DL1, to determine $\delta^{18}$O and $\delta^{17}$O. For this purpose, DL2 was temperature tuned to 7183 cm$^{-1}$ to probe the H$^{16}$OH, H$^{17}$OH, and H$^{18}$OH lines. A short term (1 hour) precision of 0.2‰ for $\delta^{18}$O and 0.5‰ for $\delta^{17}$O could be easily achieved, as shown in Fig. 4(a) and Fig. 4(b). This improvement is attributed to the better technical features of DL2 with respect to DL1, in terms of emitted power and spatial beam quality. Also, it must be noted that the gain of the pre-amplified detectors was optimized on the transmission of DL2, thus resulting in a less than optimal detection of the DL1 beam. Also in this configuration systematic errors similar to those discussed above for the experiment with DL1 were clearly present.

Subsequently, we tuned DL2 in coincidence with a pair of H$^{16}$OH and H$^{18}$OH lines at 7200 cm$^{-1}$, which exhibits the important features of having a low temperature dependence and being well resolved and isolated from other lines. Here, we found an interesting result, which is shown in Fig. 4(c). The mean $\delta^{18}$O value was 0.1‰, with a standard deviation of 0.2‰. The much better performance with respect to the oxygen isotope ratio measurements at 7183 cm$^{-1}$, using the same laser, confirms our hypothesis of line overlap as a major source of systematic errors in the $\delta^{17}$O and $\delta^{18}$O measurements at 7183 cm$^{-1}$.

Fig. 4. Examples of $\delta^{18}$O and $\delta^{17}$O measurements by means of DL2. The short-term reproducibility was found to be 0.2‰, 0.5‰, and 0.1‰, respectively for the data set plot in a), b), and c).
4. Conclusions

We have demonstrated that dual-wavelength diode laser spectroscopy enables the simultaneous determination of ²H/¹H, ¹⁷O/¹⁶O, ¹⁸O/¹⁶O isotope abundance ratios in water. Precision levels are better than those achieved in previous experiments with a color center laser at 2.7 µm. Herewith, laser spectrometry becomes a viable alternative to conventional IRMS, particularly for deuterium, and considering the laser spectrometry advantages of fast and direct measurements on water samples, no sample pretreatment, and a small and relatively cheap instrument. Preliminary tests of the reproducibility upon injection of fresh samples, performed in different spectral regions, revealed that δ¹⁸O and δ²H measurements can be carried out with systematic errors smaller than 1‰, in the spectral windows around 7200 and 7198 cm⁻¹, respectively. On the other hand, δ¹⁷O and δ¹⁸O determinations performed at 7183 cm⁻¹ require a correction of the apparent δ-values based on the measured line width difference between sample and reference gas, or an altogether different data analysis procedure, in order to arrive at the same level of accuracy, due to the partial overlapping of H¹⁶OH and H¹⁷OH lines (which enhances differential temperature and pressure effects in our current data analysis strategy). More measurements on samples, that cover a range of isotopic abundances, including standard materials back-traceable to international standards, are required in order to calibrate the instrument and truly assess its accuracy.

Acknowledgments

Livio Gianfrani is grateful to NWO (Nederlandse Organisatie voor Wetenschappelijk Onderzoek) for a NATO Visiting Scientist Fellowship. Authors thank Mauro Giuntini and Marco De Pas for their technical support related to the diode laser drivers.