

# Modulation cancellation method for isotope $^{18}\text{O}/^{16}\text{O}$ ratio measurements in water

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**Abstract:** The application of an innovative spectroscopic balancing technique to measure the isotope  $^{18}\text{O}/^{16}\text{O}$  ratio in water vapor is reported. Quartz enhanced photoacoustic spectroscopy has been employed as the absorption sensing technique. Two isotope absorption lines with the same quantum numbers, with very close lower energy levels, have been selected to limit the sensitivity to temperature variations and guarantee identical broadening as well as relaxation properties. The sensitivity in measuring the deviation from a standard sample  $\delta^{18}\text{O}$  is 1.4‰, in 200 sec of integration time.

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OCIS codes: (280.3420) Laser sensors; (140.3070) Infrared and far-infrared lasers.

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## 1. Introduction

Isotopic composition measurements of a chemical species require determining deviation of the concentration ratio  $R$  of two related isotopes from the ratio in a reference sample  $R_{st}$ . The most common application where such measurements are required is isotopologue abundance quantification. These measurements provide information about the sample origin, can be used for process identification or as a tracer. This is especially important in atmospheric climate and ecosystem research, volcanic emission studies and medical diagnostics [1–9]. For isotopologue abundance quantification, the isotopic ratio is expressed in a  $\delta$ -notation as a deviation from the reference ratio:

$$\delta[\text{‰}] = \frac{R - R_{st}}{R_{st}} \times 1000 \quad (1)$$

For isotopic characterization of samples, practically important values of  $\delta$  range from  $\sim 0.1\text{‰}$  to  $1\text{‰}$ . Making such precise measurements is difficult due to the small variations in pressure, laser power and other external factors. The most common instrument for this type of measurements is a mass-spectrometer (MS). A MS provides the required precision and accuracy, but there are a number of shortcomings associated with this technology. Mass spectrometers are expensive, bulky and in general cannot be used in field applications. Moreover, a MS cannot discriminate between molecules or molecular fragments with identical masses. In addition, a MS is not compatible with condensable gases, such as water, due to instrumental limitations. Thus isotopic analysis of water requires sample pretreatment that can potentially affect the isotopic composition. Infrared molecular absorption spectroscopy is considered as a viable alternative to MS. Current optical instrumentation for determination of isotopic composition is based on precise measurements of the peak absorption or the integrated absorbance signals of lines corresponding to two isotopes with a subsequent numerical comparison [7–9]. Hence, a small difference between isotopic compositions of the analyzed sample and the reference sample is determined as a small difference between two large numbers (concentration ratios). Sources of errors of such an approach are: the temperature and pressure dependence of the absorption line strength; non-linearity of laser tuning; baseline distortions caused by spurious interference fringes and far

wings of the irrelevant strong absorption lines; and isotopic fractionation in the sampling procedure. To address these issues, we have developed a novel spectroscopic technique, the modulation cancellation method (MOCAM) that relies on the *physical* cancellation of the measured sensor response if  $R = R_{st}$  [10–12]. In this case, the signal from the analyzed sample will be directly proportional to the deviation of the absorption line strength ratio from the reference ratio.

## 2. Experimental setup

For proof of concept of the use of MOCAM for isotopologue abundance quantification, we employed quartz enhanced photoacoustic spectroscopy (QEPAS) in a  $2f$  wavelength modulation mode [13] as an absorption sensing technique and water vapor as a test analyte. There is a strong interest in water isotopic ratio measurement, since the stable isotopes of water are effective tracers to investigate the hydrological cycle, ecological processes or paleoclimatic archives. The natural abundance ratio of isotopic water is 99.756: 0.039: 0.205 for  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{17}\text{O}$  and  $\text{H}_2^{18}\text{O}$  [14]. For our investigation, we selected the  $\text{H}_2^{16}\text{O}$  and  $\text{H}_2^{18}\text{O}$  isotopologues, because in geochemistry, paleoclimatology and paleoceanography  $\delta^{18}\text{O}$ , defined as a measure of the ratio of stable isotopes  $^{18}\text{O}:^{16}\text{O}$ , is commonly used as a measure of the temperature of precipitation as well as a measure of groundwater/mineral interactions and as indicator of processes that show isotopic fractionation, such as methanogenesis [15,16].

The simplified architecture of the MOCAM-based QEPAS setup is shown in Fig. 1. A  $3f$  technique with two 99:1 fiber beam couplers and two reference tubes, each equipped with a photo-detector, are employed to lock two diode lasers, DL1 and DL2, to absorption lines belonging to two different water isotopologues, i.e.,  $\text{H}_2^{18}\text{O}$  and  $\text{H}_2^{16}\text{O}$ , as described in [13]; We used standard water vapor to fill the reference tubes. Therefore, we employed a 10 cm-long tube for  $\text{H}_2^{16}\text{O}$  (99.756%) and a 50 cm-long one for  $\text{H}_2^{18}\text{O}$  (0.205%). Line locking feedback loops are not shown in Fig. 1.

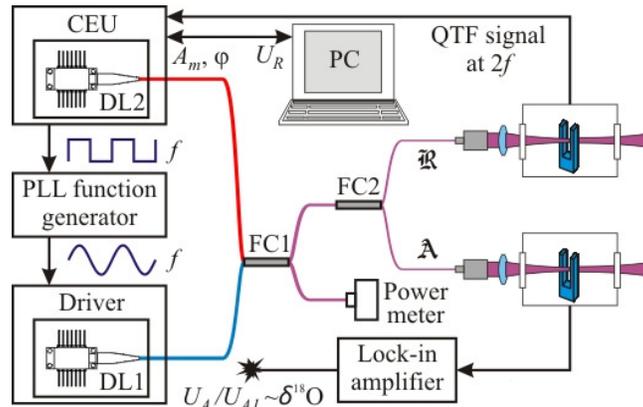


Fig. 1. Schematic of the QEPAS-based MOCAM setup. QTF – quartz tuning fork; FC1, 2 – 50:50 optical fiber couplers; CEU-control electronics unit.  $f$  – synchronization signal from CEU.

Both lasers are modulated via a sinusoidal current dither at the same frequency. We select a frequency  $f \approx (f_R + f_A)/4$ , where  $f_R$  and  $f_A$  are resonant frequencies of the two spectrophones, labeled as “Reference” (R) and “Analyzer” (A). The DL2 is mounted inside the control electronics unit (CEU) and driven by it. The CEU triggered the phase lock loop (PLL) function generator, which produces the modulation signal for DL1. The two laser beams were combined using 50:50 optical fiber couplers (FC1 OZ Optics model Fused-12-1300/1550-9/125-50/50-3A3A3A-1-0.5). Half of the optical power was used to monitor the lasers operation and check that the optical power fluctuations remain negligible for all the

measurement time. Subsequently the optical emission was directed to a second 50:50 optical coupler (FC2), and the two final beams were focused into the reference and analyzer QEPAS cells. The modulation phase  $\phi$  and amplitude  $A_m$  are set in such a way that the QEPAS signals at  $2f$  produced in the reference cell by the two lasers are opposite in phase and cancel each other. The detected signal  $U_R$  from the reference sample is used as the error signal in a computer controlled feedback loop, which continuously adjusts modulation amplitude  $A_m$  for DL1 to keep  $U_R$  constant (ideally, zero).

MOCAM measurements do not require exact 50:50 power split at FC2. However, for ideal experimental conditions it is necessary that FC2 divides radiation of DL1 and DL2 between R and A channels identically. Unfortunately, the evanescent wave fiber coupler used in our experiments was wavelength selective and did not fully satisfy that requirement. The consequences of that will be described and discussed in the following sections.

### 3. Isotopic composition calculation

The signal produced by the reference cell under balanced conditions will be:

$$U_R = k_R \left( P_1 [H_2^{18}O]_R - P_2 [H_2^{16}O]_R \right) = 0 \pm \sigma_R \quad (2)$$

where  $\sigma_R$  is the QTF thermal noise in the reference channel and  $k_R$  describes the responsivity of the spectrophone.  $P_{1,2}$  is the optical power of DL<sub>1,2</sub>.  $[H_2^{18}O]_R$  and  $[H_2^{16}O]_R$  are two water isotopologue concentrations in the reference cell, The following equation is derived from Eq. (2):

$$P_2 = P_1 \frac{[H_2^{18}O]_R}{[H_2^{16}O]_R} \pm \frac{\sigma_R}{k_R [H_2^{16}O]_R} = P_1 R_R \pm \frac{\sigma_R}{k_R [H_2^{16}O]_R} \quad (3)$$

where  $R_R = [H_2^{18}O]_R/[H_2^{16}O]_R$  is the isotopologue concentration ratio in the reference cell.

The signal from the absorption cell is:

$$\begin{aligned} U_A &= k_A \left( P_1 [H_2^{18}O]_A - P_2 [H_2^{16}O]_A \right) \pm \sigma_A \\ &= k_A \left( P_1 [H_2^{18}O]_A - P_1 R_R [H_2^{16}O]_A \right) \pm \frac{k_A [H_2^{16}O]_A}{k_R [H_2^{16}O]_R} \sigma_R \pm \sigma_A \\ &= k_A P_1 [H_2^{16}O]_A \left( \frac{[H_2^{18}O]_A}{[H_2^{16}O]_A} - R_R \right) \pm \frac{k_A [H_2^{16}O]_A}{k_R [H_2^{16}O]_R} \sigma_R \pm \sigma_A \\ &= k_A P_1 [H_2^{16}O]_A R_R \left( \frac{R_A - R_R}{R_R} \right) \pm \frac{k_A [H_2^{16}O]_A}{k_R [H_2^{16}O]_R} \sigma_R \pm \sigma_A \end{aligned} \quad (4)$$

where  $[H_2^{18}O]_A$  and  $[H_2^{16}O]_A$  are the two water isotopologues concentrations in the analyzer cell and  $R_A = [H_2^{18}O]_A/[H_2^{16}O]_A$  is the related concentration ratio.

Assuming that the QEPAS spectrophones are similar ( $k_R \approx k_A = k$  and  $\sigma_R \approx \sigma_A = \sigma$ ) and considering a small variation of  $H_2^{16}O$  concentration ( $[H_2^{16}O]_A \approx [H_2^{16}O]_R = [H_2^{16}O]$ ), we obtain:

$$\begin{aligned} U_A &= k P_1 [H_2^{16}O] \cdot R_R \cdot \delta^{18}O \cdot \frac{1}{1000} \pm \sigma_R \pm \sigma_A = \\ &= U_{A1} \cdot R_R \cdot \delta^{18}O \cdot \frac{1}{1000} \pm \sqrt{2} \sigma \end{aligned} \quad (5)$$

where  $U_{A1} = kP_1[H_2^{16}O]$  is the signal generated by the DL2 (resonant with  $H_2^{16}O$  absorption line) when DL1 is inactive (for example, its modulation disabled).  $R_R$  is known because the reference cell is filled with a calibrated sample. The  $2^{1/2}$  coefficient reflects the fact that the noise of the two spectrophones is uncorrelated and therefore adds up in quadrature. Thus the deviation of the sample isotopic composition from reference  $\delta^{18}O$  is expressed by the following equation:

$$\delta^{18}O = \frac{U_A}{U_{A1}} \frac{1000}{R_R} \quad (6)$$

In case of a natural  $^{18}O$  abundance  $R_R \approx 1/500$ , it can be seen that for perfect balancing and with small  $\delta^{18}O$ , errors in  $\delta^{18}O$  are primarily determined by a weak signal  $U_A$ . In case of QEPAS, fluctuations of  $U_A$  are determined by thermal noise of the QTF. The unbalanced signal  $U_{A1}$  is much stronger, and its instability is primarily determined by the laser power fluctuations. However, these fluctuations are transferred to  $\delta^{18}O$  as its *relative* error. In contrast, for the traditional approach of separate measurements of two absorption lines power fluctuations impact the *absolute* error. For example, if  $\delta = 10\text{‰}$  which must be known to a 0.1‰ precision (1% relative error), MOCAM requires 1%  $U_{A1}$  error, which means 1% laser power stability. Traditional approach requires 0.1‰ =  $10^{-4}$  stability for the same conditions.

If balancing is not perfect (as is the case in our experiments), then Eq. (6) changes to

$$\delta^{18}O = \frac{U_A + U_{off}}{U_{A1}} \frac{1000}{R_R}. \quad (7)$$

where  $U_{off}$  is an unbalanced offset proportional to the laser power. This offset decreases the theoretical MOCAM sensitivity.

#### 4. Results and discussion

The temperature dependence of  $\delta^{18}O$  is proportional to the difference of ground-state energies  $\Delta E$  of the selected isotope transitions [17]:

$$\frac{\Delta\delta}{\Delta T} \approx \frac{\Delta E}{kT^2} \cdot 1000 \quad (8)$$

where  $k$  is the Boltzmann constant and  $T$  is the absolute temperature. Thus, the selection of absorption lines for a pair of isotopes require that the related lower energy levels are as close as possible, to limit the sensitivity of the measurement to temperature variations, and also that they have the same quantum numbers, so as to guarantee identical broadening and relaxation properties. The concentration ratio  $^{16}O/^{18}O$  being  $\sim 500$  in standard water, we must select  $H_2^{18}O$  lines with high absorption strength. Based on these criteria we identified two absorption lines, positioned at  $7340.209 \text{ cm}^{-1}$  and  $7319.879 \text{ cm}^{-1}$ , respectively for  $H_2^{16}O$  and  $H_2^{18}O$ . The wavenumber (WN), the line strength (LS), the low state energy ( $E_2$ ), the air broadening and self-broadening coefficients (HWHM per 1 atm) of the selected lines are reported in Table 1 [18]. Pressure broadening coefficients are identical, according to the HITRAN database. The two lines are  $\sim 20 \text{ cm}^{-1}$  apart and do not overlap at the working pressure of 20 Torr (0.026 atm) of pure  $H_2O$  vapor. At a room temperature of 296 K the temperature dependence of  $\delta^{18}O$  from Eq. (8) is  $\Delta\delta/\Delta T \approx 0.022 \text{ ‰/K}$ .

**Table 1. Main parameters of the selected isotopic absorption lines**

	WN (cm <sup>-1</sup> )	LS (cm/mol)	E <sub>2</sub> (cm <sup>-1</sup> )	HWHM- air (cm <sup>-1</sup> )	HWHM- self (cm <sup>-1</sup> )
H <sub>2</sub> <sup>16</sup> O	7340.209	1.044·10 <sup>-20</sup>	212.156	0.0924	0.45
H <sub>2</sub> <sup>18</sup> O	7319.879	1.045·10 <sup>-20</sup>	210.799	0.0924	0.45

The optical powers of DL1 and DL2 passing through the two spectrophones were 5.6 mW and 1 mW, respectively. We employed sealed QEPAS cells with a volume of ~1.3 cm<sup>3</sup>. Before each measurements we evacuated the two cells to remove any residual water. Next we filled the cells with water vapor samples, sealed them and performed the measurements at room temperature at a corresponding saturated vapor pressure of 20 Torr. The resonance frequencies for the two QTFs must be as close as possible, since the two lasers must be modulated at the same frequency and this frequency must fall within the resonance curves of both QTFs. Since the resonance curves of QTFs are very narrow (< 1 Hz) at 20 torr, spectrophones with a bare tuning fork, i.e. without micro-resonator (MR) tubes were used, since adding a MR to a QTF can result in a shift of several Hz of the QTF resonant frequency [19]. The resonance frequency of the reference spectrophone was 32.763,80 Hz, while that of the sample spectrophone was 32.763,17 Hz. The FWHM of the two resonance curves [20] was ~0.65 Hz, so that the two bandwidths overlapped. Therefore we chose to drive the lasers at half of the average resonant frequency of 32.763,48 Hz (f=16381.74 Hz), because the laser frequency crosses the absorption lines twice per cycle.

Initially, both R and A spectrophones contain the same reference water sample, and the signal from R was balanced out. However, it was observed that the signal measured from the lock-in amplifier from A was not zero for these conditions, because of the wavelength selectivity of FC2. The unbalance was ~12 μV corresponding of ~4% of the full DL1-induced signal. Therefore, we re-adjusted  $A_m$  to set the signal in the A channel equal to zero. This procedure resulted in a non-zero  $U_R$  signal, and a computer-controlled feedback loop was set to maintain this signal at constant level. In this way Eq. (6) remains valid, although sensitive to variations of laser power in the reference channel. Next we filled the A cell with calibrated water samples and compared the estimated  $\delta^{18}\text{O}$  with that obtained using Eq. (6), thus measuring  $U_{A1}$  by disabling the modulation of DL1 and  $U_A$  with the modulation of both laser enabled. We used two different water samples, the first containing 99.9985% of H<sub>2</sub><sup>16</sup>O and 0.0015% H<sub>2</sub><sup>18</sup>O; the second sample was composed of 90% of H<sub>2</sub><sup>16</sup>O and 10% of H<sub>2</sub><sup>18</sup>O. Both samples were H<sub>2</sub><sup>17</sup>O depleted. In the first case we measured with a 1 sec integration time a value for  $\delta^{18}\text{O} = -896 \pm 4.8 \text{ ‰}$ , while the expected one is  $-927 \text{ ‰}$ . The ~3% difference between the two values is mainly due to the residual H<sub>2</sub><sup>18</sup>O, that is not completely removed by the evacuation procedure. For the second sample we obtained a good correlation between the expected and measured values for  $\delta^{18}\text{O}$ . We measured  $\delta^{18}\text{O} = 52900 \pm 260 \text{ ‰}$ , with a relative deviation of 0.3% from the expected value of 53068 ‰. Besides random errors related to the laser power and balancing fluctuations, our result contains systematic error because of dilution of the isotopically enriched water vapor sample by residual moisture in the gas system.

To determine the best achievable detection sensitivity of the MOCAM-based QEPAS isotope concentration sensor we performed an Allan variance analysis [21], measuring and averaging sensor response under balanced conditions. The Allan plot is shown in Fig. 2. For a 200s averaging time we achieved a minimum detection error of ~1.5 ‰ for  $\delta^{18}\text{O}$ .

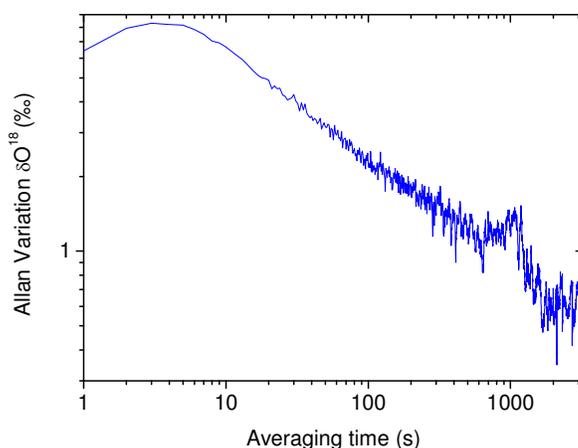


Fig. 2. Allan deviation of the  $\delta^{18}\text{O}$  as a function of integration time.

The main sources of error result from laser power fluctuations. The feedback loop for balancing is based on a Labview control program with  $\sim 1$  Hz bandwidth. The initial growth from 1 to 4s reflects delay and the related oscillations in the feedback loop when balancing the signal of the reference channel. The program will set a small limit window. When the error signal is outside of the limit window, the modulation voltage will be automatically adjusted by sending a command signal to the CEU to either increase or decrease the minimum step size of 0.01 V in order to adjust the error signal within the limit window and maintain the reference channel balanced. The resolution of the 0.01 V for modulation voltage and 1 Hz correction frequency limit the feedback loop performance. If a faster, continuous PID real-time control feedback loop is available instead of a digital correction method with a limited window setting, it will compensate the temporal variation of the laser power and further lower the noise level. Another source of error results from the non-optimal configuration since the signal in the R channel is not zero but exceeds the thermal noise of by a factor 2 (the thermal noise is  $6.4\mu\text{V}$ ) in a 0.785 Hz detection bandwidth, which is set by the internal CEU digital filters and is applicable when the data are read every 1 s without additional averaging.

The theoretically achievable sensitivity for isotopic measurements is determined from the SNR for the  $U_A$  signal, since the error derived from  $U_{A1}$  measurements results negligible with respect to that determined by  $U_A$ , being the  $U_{A1}$  signal much larger than  $U_A$ . The technical limit of  $\text{SNR}/2^{1/2}$  for the used control electronic unit (CEU) is  $\sim 10^4 \text{ Hz}^{-1/2}$ , corresponding to an error in  $\delta = 0.1 \text{ ‰}$  for a 1 Hz bandwidth. Possible ways to improve the achievable sensitivity is to employ lasers capable of higher laser output power. Furthermore, due to not perfectly matching between the laser and the 99:1 fiber splitter, we lose half of the lasers power. Hence, by improving the laser-fiber coupling in our setup we can reach a 1 ‰  $\delta$ -value. An additional improvement can be obtained by using spectrophones employing QTFs equipped with MR. We previously demonstrated up to a factor of 30 improvement of the SNR with respect to spectrophones using bare tuning forks [19], however, great care has to be taken to match the resonance frequencies of the two R and A cells within the resonance curves of both QTFs.

### Acknowledgments

The Rice University Laser Science Group acknowledges financial support from a National Science Foundation ERC MIRTHER award and a grant C-0586 from The Welch Foundation. V. Spagnolo acknowledges financial support from the Regione Puglia “Intervento Cod. DM01, Progetti di ricerca industriale connessi con la strategia realizzativa elaborata dal Distretto Tecnologico della Meccatronica” and the II Faculty of Engineering of the Politecnico di Bari.