In-line optical subtraction using a differential Faraday rotation spectrometer for $^{15}$NO/$^{14}$NO isotopic analysis

Eric J. Zhang, 1,2* Daniel M. Sigman, 3 Gerard Wysocki 1

1 Department of Electrical Engineering, Princeton University, Princeton, NJ 08544, USA
2 IBM Thomas J. Watson Research Center, Yorktown Heights, NY 10598, USA (current affiliation)
3 Department of Geosciences, Princeton University, Princeton, NJ 08544, USA

*Corresponding author: eric.jh.zhang@ibm.com

Compiled: March 22, 2021

We present a dual-modulation Faraday rotation spectrometer with in-line optical subtraction for differential measurement of nitric oxide (NO) isotopologues. In-situ sample referencing is accomplished via differential dual-cell measurements, with 3.1 ppbv-Hz$^{1/2}$ ($^{15}$NO) sensitivity through 15 cm optical path length. Our system operates at 1.9$\times$ the shot-noise limit, with a minimum fractional absorption of 1.8$\times$10^{-7} Hz$^{1/2}$. Differential measurement of both $^{14}$NO and $^{15}$NO are shown, yielding ~20 dB magnetooptical suppression. Noise analysis demonstrates stability of the differential signal up to ~500 s, with normalized ratiometric precision of 3.0 $\%\nu$Hz$^{1/2}$ using 1 ppbv $^{15}$NO (or 272 ppbv $^{14}$NO at natural abundance). We rigorously model our differential method and demonstrate the utility of in-line calibration for precise isotopic ratiometry.

Precision isotopic analysis of nitric oxide ($^{14}$NO, $^{15}$NO) and of related nitrogen forms is an emerging technique for medical and environmental diagnostics [1–4], as various biological and geochemical pathways exhibit isotopic fractionation [2, 4]. In biochemical applications, isotopic analysis may be used to identify signaling pathways [3] and pathologies via human metabolic studies [4], while environmental applications include analysis of nitrogen isotopes to determine anthropogenic contributions in global nitrogen cycling dynamics [1, 5, 6]. State-of-the-art techniques rely on isotope-ratio mass-spectrometry (IRMS) [7], thus limiting their use due to significant instrumentation and cost overhead. Sub-permil ($\%\nu$) level precision is required to assess isotopic variations in environmental samples in order to investigate many of the processes of interest, be they natural [8] or anthropogenic [9]. Therefore, the demands for precision and accuracy are high, necessitating, for example, frequent referencing to well-defined isotopic standards. The challenge is to provide precise and calibrated isotopic analysis without the cost and instrumentation overhead of IRMS systems. NO is a particularly valuable target for the development of isotopic methods as many other important nitrogen forms can be converted into it [10].

Laser spectroscopy has garnered broad interest for the detection of isotopologues due to measurable shifts in rovibrational energies arising from atomic mass variations [11, 12]. However, spectral contamination due to interfering molecular species (e.g. H$_2$O and volatile organic compounds) imposes strict sample purity requirements for accurate quantification. In cases where the analyte exhibits paramagnetism (as is the case for detection of a variety of free radicals common in chemical processes), Faraday rotation spectroscopy (FRS) has been utilized to ensure immunity against non-paramagnetic species that reside within its spectral vicinity [13–17]. This combination of spectral and paramagnetic selectivity ensures highly accurate species discrimination, and FRS has found increasing utilization in the measurement of chemical radicals in applications ranging from breath analysis [14] to environmental detection [15, 16] and even studies of fuel oxidation rates in combustion diagnostics [17]. At present, state-of-art FRS systems are able to achieve a minimum detectable polarization rotation (“noise equivalent angle”) of $\theta_{neq}$ ~ 10^{-10} rad Hz$^{1/2}$, which corresponds to performance typically in the range of 1~2$\times$ the fundamental shot-noise limit.

A variety of FRS techniques have been developed to reach ultrasensitive limits required for free-radical detection [13, 15, 18]. Dual-modulation (DM-FRS) of both magnetic field and laser frequency has proven effective in mitigating both spectral contamination (e.g. optical etalons) and low-frequency noise [14, 16]. Previously, DM-FRS was utilized for time-multiplexed isotopic studies of NO, yielding sub-permil precision [13, 16, 19]; however, ratiometric accuracy remains challenging and is predicated on the assumption that reference and sample measurements are acquired identically. Ideally, in-situ calibration should be performed to ensure that sensor drift does not impact the ratiometric result over time. Here, we present a differential DM-FRS (dDM-FRS) sensor with in-line optical polarization subtraction of sample and reference signals by reversing the sense of Faraday rotation. The in-situ calibration process avoids ratiometric offsets associated with imperfect calibration. Effective magneto-optical suppression is necessary for accurate in-line referencing which yields 19.2 dB common-mode rejection ratio (CMRR) for $^{14}$NO and ~500 s of zero-drift stability at 1.9$\times$ the shot-noise limit. The isotopic ratio is determined by measuring only the sample/reference differential signal, yielding a ratiometric precision of 3.0 $\%\nu$Hz$^{1/2}$ (normalized to 1 ppmv $^{15}$NO, or 272 ppmv $^{14}$NO at natural abundance) which may be improved with signal averaging.

The dDM-FRS system is depicted in Fig. 1, following initial developments outlined in [13, 19]. A distributed-feedback quantum cascade laser (Alpes Lasers) is employed to target the $^{15}$N$^{16}$O Q(3/2) and $^{14}$N$^{16}$O P(19/2) transitions at 1842.76 cm$^{-1}$ and 1842.95 cm$^{-1}$ respectively. Laser modulation is performed at $f_s = 50$ kHz for mitigation of low-frequency noise. The solenoid is driven sinusoidally at $f_{dr} = 100$ Hz (Behringer EPQ900) with 169 Gauss amplitude for near-optimal Zeeman splitting of the $\Delta M_z = \pm 1$ states of the $^{15}$N$^{16}$O Q(3/2) transition at an operating pressure of 80 Torr. As the beam passes through the gases with Zeeman-split transitions, relative circular birefringence is induced between the right- and left-hand circular polarizations, thereby inducing a rotation in the linearly polarized beam. Polarization measurement
occurs in a polarizer/analyzer configuration (P1 and P2 in Fig. 1(a)), where the two anti-reflection wire-grid polarizers (ISP Optics, POL-3-5-SI-25) are positioned across the sample and reference cells. Each cell is 15 cm with angled wedged-glass windows to prevent spurious back-reflections and spectral fringing. Both sample and reference cells are housed within the same solenoid to minimize magnetic field dissimilarities. The resulting optical signal is measured on a TEC-cooled MCT photodiode (Vigo PVI-3TE) and undergoes two-stage demodulation for the dual sidebands at $2\nu_f \pm \nu_{2mol}$ via phase-sensitive detection (Zurich Instruments HF2LI). Line-looked measurements are performed using the partial reflection from P1, which is sent through a high-concentration cell (2.5 vol.\% $^{15}$NO and 1.5 vol.\% $^{14}$NO), and the resulting $3f$ WMS signal is utilized to selectively lock the DFB-QCL to the $^{14}$NO or $^{15}$NO transition. Optimization of the analyzer (P2) angle is accomplished by approximately equalizing the signal relative intensity noise ($\sigma_{\text{SNR}} = 2.8 \times 10^{-12}$ Hz$^{-1/2}$) and detector noise-equivalent power ($P_{\text{neq}} = 1.15 \times 10^{-12}$ W Hz$^{-1/2}$), yielding an empirically optimized uncrossing angle of $\theta_{\text{opt}} = 25^\circ$. For an incident power (on the initial polarizer) of $P_0 = 2.0$ mW, this corresponds to 3.8 $\mu$W on the signal photodiode.

As shown in the top right inset of Fig. 1(a), optical subtraction of the signal and reference gases is accomplished by use of a retroreflector consisting of two bare-gold mirrors aligned at a relative angle of 90°. The reflection off each gold mirror causes the reversal of the ‘handedness’ of circular polarization in the beam, and the combination of two mirrors ensures the polarization sense between sample and reference cells are identical. However, the opposite magnetic field in the reference (with respect to beam direction) causes the Faraday rotation to be reversed in polarity. This yields relative concentration between the signal and reference gas cells, i.e. in-line polarization subtraction which enables in-situ calibration without requiring separate reference measurements.

Fig. 1(b) demonstrates the effect of Zeeman-splitting polarity reversal on the measured Q3(2) $^{15}$NO spectrum using gas from a certified 50 ppmv $^{15}$NO cylinder (N2 balance), which provides 184 ppmv $^{15}$NO at natural abundance (0.367 vol%). The sample (red) and reference (green) spectra were acquired by filling only one respective cell, yielding spectra of opposite polarity after signal demodulation. By filling both sample and reference simultaneously, signal subtraction may thus be performed (demonstrated in Fig. 2). The top panel in Fig. 1(b) shows the same measured spectrum for ambient air, which is effectively zero-gas at natural $^{15}$NO abundance. The absence of contaminating spectral features indicates the baseline-free nature of DM-FRS. Noise performance is assessed by line-locking to the $3f$ WMS zero-crossing of the high-concentration wavelength reference cell, yielding 195.3 nV Hz$^{-1/2}$ Gaussian-noise limited performance [13]. Based on the peak signal amplitude of $V_{\text{sig}} = 11.52$ μV in Fig. 1(b), we calculate a SNR = 59.0 Hz$^{-1/2}$ or $^{15}$NO detection limit of 3.1 ppbv Hz$^{-1/2}$, corresponding to a minimum fractional absorption ($\alpha_{\text{rel}}$) = 1.83 × 10$^{-17}$ Hz$^{-1/2}$ (see Supplement C). The minimum detectable polarization rotation (i.e. noise-equivalent angle) is $\delta_{\text{SNR}} = 1.7 \times 10^{-8}$ rad Hz$^{-1/2}$, demonstrating performance comparable to state-of-art FRS systems [13, 15, 16]. Similar measurements for optimized $^{15}$NO DM-FRS signals yields 20.3 ppbv Hz$^{-1/2}$ sensitivity [13]. Nominally, magnetic field optimization is performed to maximize the $^{15}$NO signal, resulting in a relative decrease in $^{15}$NO isotopic precision due to the sub-optimal Zeeman-split $^{15}$NO Q(3/2) transition. Nevertheless, natural abundance will yield ~270° greater concentrations of $^{15}$NO as compared with $^{14}$NO and thus the lower sensitivity to the major isotope negligibly impacts the precision of radiometric analysis.

To demonstrate real-time optical polarization subtraction, a multi-stage line-looked measurement is depicted in Fig. 2(a), whereby the sample and reference gas cells are filled individually and then concurrently during successive DM-FRS acquisition sequences. Between ~200 to 600 s, only sample gas is measured (184 ppbv $^{15}$NO), yielding a positive DM-FRS signal with amplitude $^{15}$NO $\delta_s = 11.61$ μV (averaged over the step duration), and is similar to Fig. 1(b). Between ~850 to 1150 s, the identical gas is flown through only the reference cell, yielding a measured amplitude of $^{15}$NO $\delta_s = -11.21$ μV. The negative sign is measured directly after demodulation and is indicative of the opposite Zeeman split polarity of the $\Delta M = \pm 1$ states. The difference between sample and reference signal magnitude is primarily attributable to path length variations of the customized gas cells, which is within the glassware fabrication error. Between ~1150 to 1400 s, both sample and reference cells are filled simultaneously, resulting in the optical difference $^{15}$NO $\delta_s = 0.43$ μV. A null measurement is performed from 1500 s onwards, yielding $V_0 = 95$ nV and is used as the zero-gas baseline of our system. This minor non-zero deviation is a consequence of electromagnetic interference (EMI) from the solenoid, which may be reduced by improved high magnetic permeability shielding of the laser and cabling in future design iterations. To ascertain the magneto-optical common mode rejection ratio (CMRR), we account for this null offset in each of the measured signals, i.e. $^{15}$NO $\delta_s = [^{15}$N]s $\rightarrow [^{15}$N]s $- V_0$ [15$^N$]s $- V_0$ which yields a $^{15}$NO suppression factor.
sample difference measurements, and therefore in-situ real-time calibration. In what follows, our goal is to rigorously demonstrate the benefit of in-line referencing and we derive an expression for the isotopic ratio based on sample/reference differential signals $^{15}j$ and $^{15}j$. We begin from the definition:

$$
\delta^{15}N(t) = \left( \frac{\left[ ^{15}N(t) \right]}{\left[ ^{15}N(t) \right]} - 1 \right) \times 10^3 \ \%_o
$$

(2)

where $k_{15}$ and $k_{14}$ correspond to relative sample/reference detection sensitivities for $^{15}$NO and $^{15}$NO respectively and are ideally unity when sample and reference conditions are identical. We assume that non-zero offsets ($V_\delta$) are accounted for in all measured signals. Under the assumption that $^{15}j < [^{15}N]_0$ (i.e. sample and reference $^{15}$NO are similar), we arrive at an equivalent expression (for derivations, see Supplement A):

$$
\delta^{15}N(t) = \left( 1 + \frac{1}{1 + R_{CMRR}} \right) \times 10^3 \ \%_o
$$

(3)

where we have defined (see Supplement B):

$$
R_{CMRR} = \frac{1 - k_{15}}{k_{14}} - \frac{1 - k_{15}}{k_{14}}
$$

(4)

which can be shown to be equivalent to the operational definition given in Eq. (1). $\Omega_{(t)}(t), \Omega_{(t)}(t), \Omega_{(t)}(t)$ denote terms of increasing order (decreasing significance) to $\delta^{15}$N:

$$
\Omega_{(t)}(t) = \left[ \begin{array}{l}
\left[ ^{15}N(t) \right]
\end{array} \right] - \left[ \begin{array}{l}
\left[ ^{15}N(t) \right]
\end{array} \right],
\Omega_{(t)}(t) = \left[ \begin{array}{l}
\left[ ^{15}N(t) \right]
\end{array} \right],
\Omega_{(t)}(t) = \left[ \begin{array}{l}
\left[ ^{15}N(t) \right]
\end{array} \right]
$$

(5)

The final term $\tau^{15}R_{CMRR}$ in Eq. (3) accounts for finite CMRR, which manifests as an additive offset to $\delta^{15}$N, and can be quantified through methods depicted in Fig. 2(a):

$$
\tau^{15}R_{CMRR} = \frac{\tau^{15}R_{CMRR}^{15}R_{CMRR}}{1 + \tau^{15}R_{CMRR}}
$$

(6)

Nominally, only the first-order term offset contributes to the imprecision in Eq. (3), which yields (see Supplement D) [13]:

$$
\Delta \delta^{15}N(t) = \left( 1 + \frac{1}{1 + R_{CMRR}} \right) \times \left( \frac{\Delta \gamma(t)}{\Delta \gamma(t)} \right) - \left( \frac{\sigma_{\gamma(t)}}{\sigma_{\gamma(t)}} \right) \times \left( \frac{\Omega_{(t)}}{\Omega_{(t)}} \right) \times 10^3 \ \%_o
$$

(7)

where we define $\Delta = 1.9$ as the performance factor above the fundamental shot-noise limit as shown in Fig. 2(b). Eq. 7 yields a precision of $\Delta \delta^{15}$N[\$](t) \approx 3.1 \ \%$ over $1 \ \mu$s (at $1 \ \mu$ ppm $^{15}$NO using $\sigma_{\gamma(t)} = 102.7 \ \mu$V Hz$^{-1/2}$) and is consistent with the value determined via Allan deviation analysis. Eqs. (3) and (7) indicate two key features of our dDM-FRS measurement. First, assuming we control $^{15}j < [^{15}N]_0$, and that $[^{15}N]_0$, $[^{15}N]_0$, and CMRR are known precisely (see Supplement D and E), $\delta^{15}$N depends only on $^{15}j(t)$ and $^{15}j(t)$ (Eqs. (3-6)), which was the initial goal in our differential formulation. In other words, our differential signal provides all information required to determine $\delta^{15}$N in real-time. Second, measurement uncertainties are dominated by $^{15}$j(t) and contribute only fractional errors to $\delta^{15}$N (Eq. (7)). We contrast this with temporally separate reference and sample measurements [16], where even minor variations in the reference ratio (e.g. small fractionation offsets in the gas flow system) may cause intolerable offsets in ratiometric analysis.

In the formulation of Eq. (3), we have assumed two caveats: (i) the CMRR remains stable over the measurement duration and (ii) $^{15}j < [^{15}N]_0$. In (i), the CMRR offset term $\tau^{15}R_{CMRR}$ (Eq. (6)) is identical to the $\sim 500$ s stability time derived from Allan-deviation analysis of $\Omega_{(t)}(t)$ (Fig. 2(b)); thus no recalibration is required within the zero-drift time. In (ii) the reference and sample gases must be similar in concentration. Empirically,
real-time dilution tracking may be used to ensure $^{15}$N remains adequately small and will be implemented in future system prototypes.

Fig 3(a) shows a measurement of both $^{14}$N and $^{15}$N isotopes on our dDM-FRS system with a single laser, by sequentially line-locking to the $^{15}$NO-Q(3/2) and $^{14}$NO-P(19/2) transitions [16, 19] using the $^{3}$f WMS reference photodiode signal (Fig. 3(a)). An example is shown in Fig. 3(a), which repeats Fig. 2(a) with additional line-switching at 100 s intervals, allowing measurement of time-multiplexed $^{14}$NO and $^{15}$NO signals. The line-lock time-constant is ~5 s, yielding a measurement duty cycle of 47.5% for each isotope.

To demonstrate the ratiometric precision dependence on varying NO concentration, a five-step dilution experiment is performed in Fig. 3(b), with the diluted gas flowing into both sample and reference cells. Line-locking is performed at a faster rate of 30 s intervals for higher frequency of quasi-simultaneous signal acquisition from both isotopologues. Using the different $^{14}$NO signal $\delta$N(t), we calculate $\frac{[^{15}\text{N}]}{[^{14}\text{N}]}(t)$ from our known $\tau_{\text{RMS}}$ and reference gas concentration, which is used to calculate $\frac{[^{15}\text{N}]}{[^{14}\text{N}]}$(cyan points) based on natural abundance. The different $^{15}$N(t) is measured directly (red points) and is effectively null due to the magneto-optical suppression. The top panel shows calculated $\delta$N, demonstrating progressive improvement of ratiometric precision as $^{15}$NO concentration is increased. As an experimental verification of our derived model, all terms ($\Omega_{\text{OSF}}(t)$, $\Omega_{\text{OSF}}(t)$, $\Omega_{\text{S}}(t)$ and $\tau_{\text{RMS}}$) in Eq. (3) have been utilized in the determination of $\delta$N. At 78.1 ppbv $^{15}$NO, we measure a ratiometric precision of 44%$^{\text{Calc.}}$, corresponding to a concentration-normalized precision of 3.4%$^{\text{Hz/1/2}}$ (at 1 ppmv $^{15}$NO) in good agreement with Allan deviation analysis in Fig. 2(b). In our present configuration, sample concentrations $>3.4$ ppmv $^{15}$NO will thus enable sub-permille precision for 1 s averaging time. In cases where averaging up to the instrument stability time (~500 s) is permitted, this concentration constraint is relaxed to merely $^{15}$NO $\sim$ 50 ppmv ($^{15}$NO $\sim$ 14 ppmv). Finally, we note that $\delta$N in Fig. 3(b) remains null, independent of NO concentration, indicating that our dDM-FRS system does not introduce fractionation artefacts and may therefore be effectively utilized for high-precision applications.

In our first-generation dDM-FRS prototype, we demonstrate in-situ calibrated isotopic ratiometry of NO using sample and reference differential signals. Noise analysis shows performance at 1.9× the shot-noise limit ($\sim$500 s zero-drift time), with $\delta_{\text{SNR}} = 1.7 \times 10^{-7}$ rad Hz$^{-1/2}$ and minimum fractional absorption ($\delta_{\text{MIN}}$) = 1.8 × 10$^{-3}$ Hz$^{-1/2}$ on-par with state-of-the-art FRS systems. In-line magneto-optical subtraction (CMRR $\sim$ 20 dB) is used for in-situ calibration, with 30%$^{\text{Hz/1/2}}$ ratiometric precision (normalized to 1 ppmv $^{13}$NO, or 272 ppmv $^{14}$NO). Our results show the dDM-FRS system to be free of fractionation artefacts. Isotopic ratiometry from dilution step measurements validates our in-line calibration model. Future work will focus implementation of active dilution tracking for real-time ratiometry, in addition to implementing a second laser to simultaneously measure both isotopologues and mitigate the impact of measurement duty cycling on averaging precision.

Funding. The authors acknowledge funding support from the Eric and Wendy Schmidt Transformative Technology Fund, the Walbridge Fund (Princeton Environmental Institute), and the Natural Sciences and Engineering Council of Canada.

Acknowledgments. The authors thank Q. Ji and F. Nuruzzaman for helpful discussions, and M. J. Souza for custom glassware construction.

References

1. N. Gruber, J. N. Galloway, “An Earth-system perspective of the global nitrogen cycle,” Nature 451, pp. 293–296, 2008.
2. D. M. Sigman, K. L. Karsh, K. L. Casciotti, “Ocean process tracers: nitrogen isotopes in the ocean,” In Encyclopedia of Ocean Science; Elsevier: Amsterdam, The Netherlands, 2009.
3. L. J. Ignarro, “Nitric oxide as a unique signaling molecule in the vascular system: a historical overview,” J. Physiol. Pharmacol. 53, pp. 503–514, 2002.
4. L. Castillo, L. Beaumier, A. M. Ajami, V. R. Young, “Whole body nitric oxide synthesis in healthy men determined from [15]arginine-to-[15]citrulline labelling,” P. Natl. Acad. Sci. USA 93, pp. 11460–11465, 1996.
5. M. G. Hastings, J. C. Jarvis, E. J. Steig, “Anthropogenic impacts on nitrogen isotopes of ice-core nitrate,” Science 324, pp. 1288, 2009.
6. H. Ren, Y. Chen, X. T. Wang, G. T. F. Wong, A. L. Cohen, T. M. DeCarlo, M. A. Weigand, H. S. Mii, D. M. Sigman, “21st-century rise in anthropogenic nitrogen deposition on a remote coral reef,” Science 356, pp. 749–752, 2017.
7. M. A. Weigand, J. Foriel, B. Barnett, S. Oleynik, D. M. Sigman, “Updates to instrumentation and protocols for isotopic analysis if nitrate by the densitifier method,” Rapid Commun. Mass Spect 30 (12), pp. 1365–1383, 2016.
8. X. E. Ai, A. S. Studer, D. M. Sigman, A. Martinez-Garcia, F. Fripiat, L. M. Thöle, E. Michel, J. Gottschalk, L. Arnold, S. Moretti, M. Schmitt, S. Oleynik, S. L. Jaccard, G. H. Haug, “Southern Ocean upwelling. Earth’s obliquity, and glacial-interglacial atmospheric CO_{2} change,” Science 370 (6522), pp. 1348–1352, 2020.
9. X. T. Wang, A. L. Cohen, V. Liu, H. Ren, Z. S. Gu, G. H. Haug, D. M. Sigman, “Natural forcing of the North Atlantic nitrogen cycle in the Anthropocene,” Proc. Nat. Acad. Sci. USA 115 (22), pp. 10606–10611, 2018.
10. R. S. Braman, S. A. Hendris, “Nitramon nitrate and nitrogen determination in environmental and biological materials by Vanadium(III) reduction with chemiluminescence detection,” Anal. Chem. 61 (24), pp. 2715–2718, 1989.
11. J. F. Becker, T. B. Sauke, M. Loevenstein, “Stable isotope analysis using tunable diode laser spectroscopy,” Appl. Opt. 51 (12), pp. 1921–1927, 1972.
12. M. C. Phillips, B. E. Brumfield, S. S. Haruki, “Real-time standoff detection of nitrogen isotopes in ammonia plumes using a swept external cavity quantum cascade laser,” Opt. Lett. 43 (17), pp. 4065–4068, 2018.
13. E. J. Zhang, “Noise mitigation techniques for high-precision laser spectroscopy and integrated photonic chemical sensors,” Doctoral Dissertation, Princeton University, 2016.
14. Y. Wang, M. Nikodem, E. Zhang, F. Clach, I. Barnes, S. Comhair, R. A. Dawek, C. Kao, G. Wysocki, “Shot-noise limited Faraday rotation spectroscopy for detection of nitric oxide isotopes in breath, urine, and blood,” Sci. Rep. 5, doi:10.1038/srep09096, 2015.
15. E. J. Zhang, B. Brumfield, G. Wysocki, “Hybrid Faraday rotation spectrometer for sub-ppm detection of atmospheric O_{2},” Opt. Exp. 22 (13), pp. 15957–15968, 2014.
16. E. J. Zhang, S. Huang, Q. Ji, M. Svehlikova, Y. Wang, B. Ward, D. Sigman, and G. Wysocki, “Nitric Oxide Isotopic Analyzer Based on a Compact Dual-modulation Faraday Rotation Spectrometer,” Sensors 15 (10), pp. 25992–26008, 2015.
17. B. Brumfield, W. Sun, Y. Wang, Y. Ju, G. Wysocki, “Dual modulation Faraday rotation spectroscopy of NO_{2} in a flow reactor,” Opt. Lett. 39 (18), pp. 1783–1786, 2014.
18. R. Lewicki, J. H. Doty III, R. F. Cari, F. K. Tittel and G. Wysocki, “Ultrasonic detection of nitric oxide at 5.33 μm by using external cavity quantum cascade laser-based Faraday rotation spectroscopy,” Proc. Nat. Acad. Sci. USA 106, pp. 12587–12592, 2009.
19. E. J. Zhang, D. M. Sigman, G. Wysocki, “Analysis of nitric oxide isotopes via differential faraday rotation spectroscopy,” Conference on Lasers and Electro-Optics, AT3b.3, San Jose, June 2016.