Case Study CS-LD01 Rev. A

Lower Electronic Noise Enhances Atmospheric Gas Sensing

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ABSTRACT

Researchers at the Center for Atmospheric and Environmental Chemistry at Aerodyne Research, Inc. have developed a multitude of direct absorption atmospheric trace gas measurement instruments. Relying on high-quality optics, lasers, and electronics, measurements from this research group in Billerica, Massachusetts are reaching parts-per-trillion (10^{-12}) precision, thanks in part to the integrated low-noise current drivers. This precision allows the developed instruments to be viable resources for making real-time measurements of trace atmospheric gases. The use of non-cryogenic semiconductor lasers allows the data to be collected outside of the laboratory in ambient environments.

INTRODUCTION

In order to better understand global warming, among other atmospheric topics, quantification of the amounts of gases (both major and minor) in the atmosphere is a relevant topic of study. One of the methods available is direct laser absorption spectroscopy. In particular, the advance of semiconductor lasers has enabled researchers to perform these experiments outside of the laboratory, without the requirement of cryogenic cooling, and with the benefit of operation in the region of the spectrum where many atmospheric gases have their strongest absorption profiles.

Utilizing their dual-laser instruments, the Center for Atmospheric and Environmental Chemistry at Aerodyne Research, Inc. makes high-speed, high-precision measurements of trace atmospheric gases. These instruments are designed to measure isotopologues. An isotopologue is a molecule that has zero, one, or more substitutions of a minor isotope of an atom for a major isotope of an atom [1]. Isotopes of atoms are differentiated by the number of neutrons present in the nucleus, and thus, are distinguished by the total number of nucleons. The notation used to represent isotopes is to put the total number of nucleons as a superscript to the left of the chemical abbreviation for the molecule.

The instruments take advantage of reference gas measurements, real-time temperature and pressure measurements, and comparison with HITRAN [2] data. The instruments under consideration in this paper feature a multi-pass cell, which allows for long (up to 210 m) path lengths in a relatively small container (the largest is 56 cm × 77 cm × 64 cm). The precision available for some trace gas measurements is low parts-per-trillion.

This level of precision has been aided by multiple improvements in the instrument design. The optics themselves have been improved [3], the transition from pulsed quantum cascade lasers (QCLs) to continuous wave (CW) QCLs was made [3], and significant improvement in the current driver for the QCL was integrated [1,4]. These improvements have allowed measurements of the trace atmospheric gases to improve from the parts-per-billion range [5] to the parts-per-trillion range [4].

APPROACH

Following the work detailed in [1,3-8], the researchers use semiconductor lasers (either diode, interband cascade, or quantum cascade, depending on the gas under study) for direct absorption spectroscopy. By carefully choosing a wavelength range, multiple atmospheric gases can be measured. For example, two QCLs emitting at approximately 1765 cm^{-1} and 2052 cm^{-1} allow measurements of formaldehyde, carbonyl sulfide, formic acid, and carbon dioxide simultaneously [6]. The same instrument with a different choice of lasers is also described in [6], with QCL outputs of 1277 cm^{-1} and 1283 cm^{-1}. Nitrous acid, hydrogen peroxide, nitrous oxide, and methane can be simultaneously measured with this choice of output wavelength. **Figure 1** shows an example of absorption lines for water and carbon dioxide. The instrument described in [1] allowed simultaneous measurement of seven total isotopologues of H_2O and CO_2.

Along with proper wavelength choice, the optical design of the instruments has been optimized to maximize the signal to noise ratio. The long path length enabled by the multi-pass cell increases the effective absorption of isotopologues that are weakly absorbing. By operating at reduced pressure in the multi-pass cell, effects such as line-broadening due to pressure are avoided.

Additionally, the lasers (and sometimes the detectors) need to be cooled to maintain optimal performance. The CW lasers can be cooled by thermoelectrics. Some detectors required liquid nitrogen cooling, while for others, thermoelectrics were sufficient.

Via modulation of the laser current, the wavelength was tuned continuously across the set of lines, fully extending on both sides away from the absorption profile. Extending the tuning range outside of the absorption profile allows for an accurate measurement of “light noise.” Throughout the course of the measurement, the laser current would also be tuned below threshold in order to measure “dark noise.” While acquiring data in the range where the absorption profile is strongest, the researchers measured “proportional noise.” Careful collection and analysis of these types of noise allowed the researchers to iteratively improve on the instrument’s design. Ref. [4] goes into particularly deep detail of the noise analysis performed.

- *Dark noise* is defined as the signal that is produced when the detector is blocked (or the laser is below threshold, and no light is output). It includes noise that is inherent to the detector itself, along with fundamental electronic noise.
- *Light noise* is defined as the variation of the signal that is measured when the laser is in the low absorption region of the profile. It includes the dark noise mentioned above, along with noise due to the laser and driver.
- *Proportional noise* is defined as the measured signal variation when the laser is tuned to a high absorption region of the profile. Laser driver noise and noise due to environmental conditions are examples of proportional noise.

The researchers utilized TDL Wintel software to interface with the instruments. TDL Wintel can modulate the laser current for both lasers and control the gas cell valves along with logging, averaging, and analyzing data. This software allows for operation of the instrument without direct supervision. During development, a prototype unit ran nearly continuously for 10 months while the researchers continued fine-tuning the instrument and the measurement process [7].

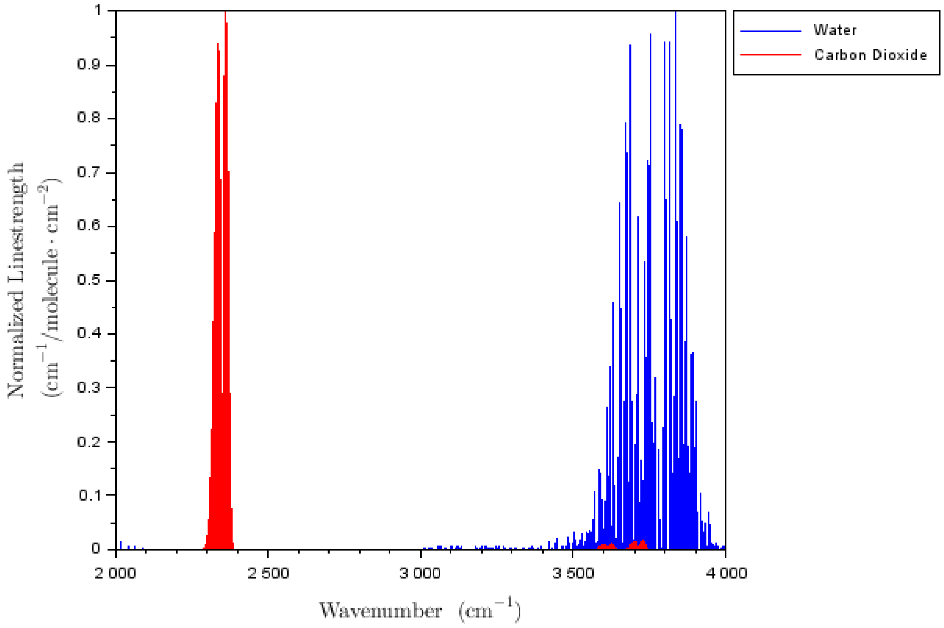

Figure 1. Normalized water and carbon dioxide (major isotopologue) absorption as a function of wavenumber. Note that in a non-normalized form, the carbon dioxide lines would be approximately an order of magnitude stronger than the water lines. Data from HITRAN.

UNDERSTANDING THE DATA

The noise data is presented in different ways, depending on what information is relevant to the application. For all of the types of noise presented below, lower values are indicative of higher precision measurements.

For applications where the value of concentration is needed, without reference to other variables, noise of the measurement is given in *parts-per* notation (e.g. parts-per-million would be represented by “ppm”, parts-per-billion would be represented by “ppb”, etc.). Equivalently, the data can be represented in scientific notation. For example, 2×10^{-6} is equivalent to 2 ppm.

Another way that noise is specified includes some information about the abundance of the gas under study. When the noise is specified by the name *absorption* and is unitless, that indicates the value given has taken the “parts-per” noise described above, and weighted it based on the ambient concentration and the absorption depth. The ambient concentration is generally given in ppb, and the absorption depth is unitless. The absorption depth indicates the probability of the molecule absorbing a photon. A higher absorption depth value suggests higher absorption probability (more likely to absorb light). The absorption measurement noise is the standard by which Aerodyne assesses good performance. Instruments are considered to have good performance if the measurement has an absorption noise of $\sim5\times10^{-6}$ in one second. [1]

Adding one final piece of information to the specification, the absorption noise can then be normalized to the experimental path length. *Absorbance* is specified in this way, and has units of inverse length (generally cm^{-1}).

A different, but related noise specification is given when the experiment is measuring isotopologues ratiometrically. In this case, the resulting noise is usually given in a *per mil* notation, which is represented by ‰. This type of specification tells the reader what amount of minor isotopologue can be accurately measured out of the ambient gas, taking into account the concentration of the major isotopologue in ambient air. An example from [1]: the researchers were able to measure the ratio of $^{13}CO_2$ (minor) to $^{12}CO_2$ (major) to the specified precision of 0.1‰. In other words, they measured changes of 0.0001 in the minor isotope of carbon dioxide. Taking into account that $^{13}CO_2$ comprises only approximately 1.1% of ambient carbon dioxide (see **Table 1**), this measurement is precise enough to allow isotopic studies of sources and sinks of carbon dioxide [8].

	MOLECULE	ABUNDANCE
Water Isotopologues	$H_2{}^{16}O$	0.997317
	$H_2{}^{18}O$	0.002000
	$HD^{16}O$	3.106930×10^{-4}
Carbon Dioxide Isotopologues	$^{12}C^{16}O_2$	0.984204
	$^{13}C^{16}O_2$	0.011057
	$^{16}O^{12}C^{18}O$	0.003947
	$^{16}O^{12}C^{17}O$	7.339890×10^{-4}

Table 1. HITRAN data for isotopologues of water and carbon dioxide that were measured in [1].

ENHANCING PRECISION

Given that noise from the current driver impacts two out of the three categories of noise defined (light and proportional noise), it is inherently important to minimize the noise from the driver. Recently [1,4], the researchers have implemented quantum cascade laser drivers from Wavelength Electronics to reduce the noise contribution from the QCL driver. This choice has resulted in "significant improvement in the performance" of their QCL-based instruments. **Figure 2** shows selected noise specifications reported by the researchers, which clearly shows the trend towards higher precision for nitric oxide (NO), formic acid (HCOOH), carbonyl sulfide (OCS), nitrous acid (HONO), nitrous oxide (N_2O), and methane (CH_4).

By implementing quantum cascade laser drivers from Wavelength Electronics, the researchers were able to lower the total noise in their measurements. By minimizing the driver's contribution to the total noise, they were able to troubleshoot other sources of electronic noise in their instruments.

With the implementation of the low-noise QCL driver, noise analysis (including Fourier transforms and Lomb power spectra, among other tools) yielded information that led to further improvement of their instruments.

In [1], it was discovered that there were three sources of excess noise that could be reconciled. First, the switching frequency of the laser driver's power supply was impacting the measurement noise. Second, an extraneous electrical signal was being input to the driver, and was thus transformed into noise. Third, interference fringes developed in the beam path that led to optical noise.

In [4], the researchers discovered a new type of noise that they had not seen before in previous iterations of their instruments. The noise found in this case was mixed (coupled) electrical and optical noise. The optical noise was again found to be due to interference fringes developing, while the source of electrical noise was narrowed down to a faulty electronics card in the instrument.

In order to do this type of extensive noise testing, the overall system noise must be low. By replacing standard laser diode drivers with Wavelength Electronics' patented low-noise QCL driver, one source of noise in the complex instrument was minimized, allowing further investigation on other components that may contribute to the overall noise in the system.

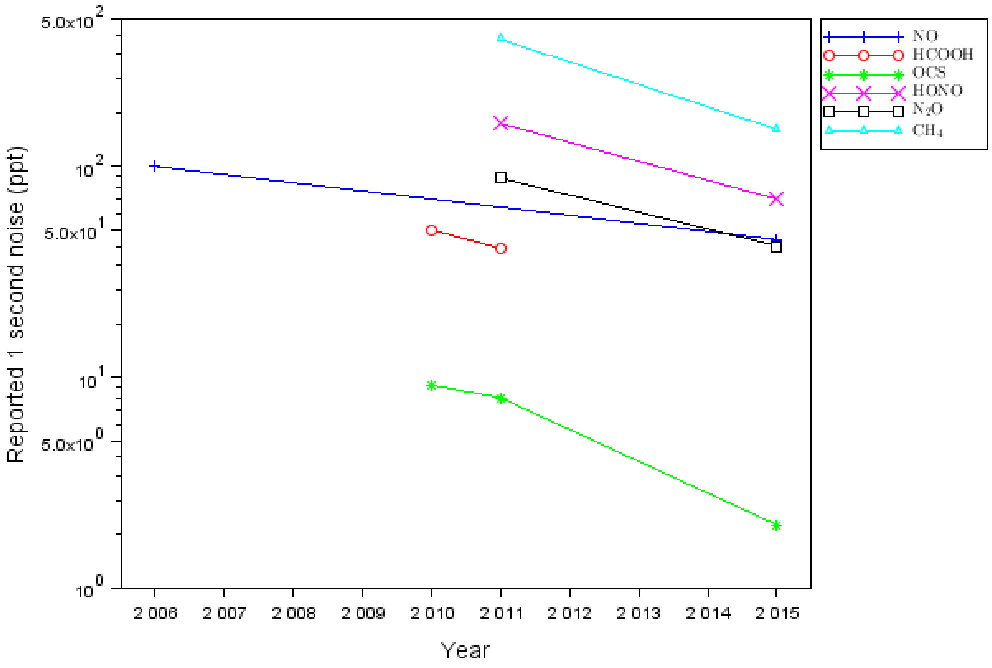

Figure 2. Noise specifications reported by the researchers in [3-6]. The downward trend towards more precision is due to improvements in the optics and the drive electronics for the QCL-based instruments.

SUMMARY

The precision gained from the low-noise Wavelength QCL driver, along with the troubleshooting efforts of the researchers has allowed Aerodyne Research, Inc. to produce trace gas instruments that can detect in the low parts-per-trillion level. This precision allows their instruments to be utilized in various research capacities, and enables scientists to further the understanding of atmospheric gas levels, and causes of their fluctuations.

USEFUL LINKS

- QCL2000 OEM
- QCL2000 LAB

REFERENCE

1. J. B. McManus, D. D. Nelson, and M. S. Zahniser, "Design and performance of a dual-laser instrument for multiple isotopologues of carbon dioxide and water," Opt. Express **23**(5), 6569-6586 (2015).
2. The HITRAN Database, *hitran.org*
3. J. B. McManus, M. S. Zahniser, D. D. Nelson, J. H. Shorter, S. Herndon, and E. Wood, "Application of quantum cascade lasers to high-precision atmospheric trace gas measurements," Opt. Eng. **49**(11), 111124 (2010).
4. J. B. McManus, M. S. Zahniser, D. D. Nelson, J. H. Shorter, S. C. Herndon, D. Jervis, M. Agnese, R. McGovern, T. I. Yacovitch, and J. R. Roscioli, "Recent progress in laser-based trace gas instruments: performance and noise analysis," Appl. Phys. B **119**(1), 203-218 (2015).
5. J. B. McManus, D. D. Nelson, S. C. Herndon, J. H. Shorter, M. S. Zahniser, S. Blaser, L. Hvozdara, A. Muller, M. Giovannini, and J. Faist, "Comparison of cw and pulsed operation with a TE-cooled quantum cascade infrared laser for detection of nitric oxide at 1900 cm^{-1}," Appl. Phys. B **85**(2-3), 235-241 (2006).
6. J. B. McManus, M. S. Zahniser, and D. D. Nelson, "Dual quantum cascade laser trace gas instrument with astigmatic Herriot cell at high pass number," Appl. Opt. **50**(4), A74-A85 (2011).
7. J. B. McManus, D. D. Nelson, and M. S. Zahniser, "Long-term continuous sampling of $^{12}CO_2$, $^{13}CO_2$, and $^{12}C^{18}O^{16}O$ in ambient air with a quantum cascade laser spectrometer," Isotopes Environ. Health Stud. **46**(1), 49-63 (2010).
8. D. D. Nelson, J. B. McManus, S. C. Herndon, M. S. Zahniser, B. Tuzson, and L. Emmenegger, "New method for isotopic ratio measurements of atmospheric carbon dioxide using a 4.3 μm pulsed quantum cascade laser," Appl. Phys. B **90**(2), 301-309 (2008).

KEYWORDS

quantum cascade laser, QCL, low noise, current driver, absorption, direct absorption spectroscopy, parts-per-billion, parts-per-trillion, multi-pass cell, atmospheric trace gas, isotopologue, isotope

REVISION HISTORY

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REVISION	DATE	NOTES
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