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Interactive comment on "Open-path, quantum cascade laser-based sensor for high resolution atmospheric ammonia measurements" *by* D. J. Miller et al.

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Responses to Anonymous Referee #2:

Comment: This paper is interesting, nicely written, and should be published. I believe comments on the following would add to the paper.

Response: We are grateful for the constructive comments and useful suggestions of Anonymous Referee #2. Below are detailed explanations of the changes to improve the originally submitted manuscript in response to all comments.

Comment: 1) Details of the following âËŸA ′c Laser tuning range used for ammonia

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measurements. âËŸA ′c Maximum tuning range possible with this laser. âËŸA ′c What modulation index was used for open path studies?

Response: We add the following to the revised manuscript (section 2): The QC laser tuning range for NH3 measurements is 0.52 cm-1, based on the current tuning rate at 50 Hz ramp frequency. The maximum current tuning range from threshold to maximum current is ∼160 mA at laser operating temperature (19°C). The current tuning rate decreases with increasing modulation frequency, as demonstrated by Tao et al. (2012a). We use a modulation amplitude comparable to the ramp amplitude. In practice, the maximum tuning rate is limited by attenuation of the current near the current limit, a safety feature of the QCL500 current driver. We have modified this section as follows:

"The QC laser tuning range for NH3 measurements is 0.52 cm-1, based on the current tuning rate at 50 Hz ramp frequency. Tao et al. (2012a) demonstrated that for the QC laser used here, the current tuning rate decreases with increasing ramp or modulation frequency. Although higher ramp and modulation frequencies should improve sensitivity by minimizing laser excess noise, the decrease in tuning rate at higher frequencies, the broad spectral features probed, and practical QC laser tuning rate limitations prevent us from going to higher frequencies. The tuning rate limitations allow us to achieve a modulation index of ∼1.4 for NH3 measurements, which is not at the most sensitive, optimal 2.2 value [Reid and Lebrie, 1982]."

Finally, we also add the following to the revised manuscript (section 5): ". . .we achieve a modulation index of ∼1.4 for NH3 measurements."

Comment: 2) Figure (1), page 7029, shows a transmission version of the Herriot cell. This configuration is more sensitive to thermal and other mirror movement than the conventional Herriott cell. Why did the authors chose the transmission configuration?

Response: We use a configuration with laser and detector components on opposite sides of the optical cell for practical opto-mechanical component design considerations, as explained in the revised manuscript (section 2.1) and to separate the output beam

from input beam to reduce interference fringing. We use a Herriott cell configuration where the last (N-1)th spot exits the back mirror hole, which is 90 degrees separated from the front mirror input hole. We have tested the system extensively under temperature cycling (as noted in the original manuscript, section 4) and mounted the sensor on a moving vehicle with vibrations, achieving >7000 km of mobile NH3 measurements. As noted in the manuscript (section 4): "...field deployments led to improvements in the opto-mechanical design to address temperature cycling effects on the alignment, laser thermal stability and detector temperature control." Although the conventional Herriott cell version may produce even more stable results, our transmission design is robust in terms of stable light intensity on the detector under the field conditions tested.

Comment: 3) The ramp frequency of 50Hz is unusually low. A higher current ramp frequency would probably improve S/N. Page 7010 (lines 15-16).

Response: We use 50 Hz to achieve a higher current tuning rate [Tao et al., 2012a]. WMS detection allows us to shift our detection to 15 kHz, which minimizes 1/f noise at lower detection frequencies. Although sweeping the laser faster will in theory improve S/N, as we ramp at higher frequencies, the current tuning rate decreases, which would prevent a laser scan over the entire absorption features of interest [Tao et al. 2012]. To clarify, as noted above (see response to comment 1), we now describe why we do not use higher modulation frequencies and amplitudes with the given QCL.

Comment: 4) Low power consumption is one of the stated benefits of their experiment. Page 7008 (Lines18-20) A sensitive pulsed QCL based WMS technique has been demonstrated [Manne J. et.al, Applied Optics, Vol. 50 Page E112 (2011)] and of course pulsed laser operation may consume less power than a CW laser operation.

Response: The pulsed QCL-based WMS technique mentioned [Manne et al., 2011] uses a closed-path configuration for detection of acrylonitrile. Manne et al. (2011) note that: "Pulsed QC lasers are typically used with 1% to 2% duty cycle so the power consumed is a small fraction of that used by a cw device." Pulsed operation does

consume overall less power than CW operation. However, for open-path detection, we are concerned with lower power consumption relative to systems that require gas handling systems (pumps) and whole system temperature control for field operation. Our sensor's main difference from previous sensors is the elimination of these pumps, gas handling and whole system temperature control systems. These components add hundreds of Watts to the system (as mentioned on page 3, lines 22-23). The difference in total power consumption between pulsed and CW-DFB QC lasers is on the order of single Watts, which is at least an order of magnitude lower than the difference between a closed-path system requiring a pump and our open-path system (difference of hundreds of Watts). In addition, CW-DFB QC lasers have other advantages over pulsed QC lasers, including narrower laser line-width for higher spectral resolution and measurement selectivity [Tittel et al., 2003] and avoid pulse to pulse intensity fluctuations, allowing for higher detection sensitivity. Although pulsed DFB-QCLs are easier to fabricate, CW-DFB QC lasers operating at room temperature are readily available (e.g. Alpes Lasers). Incorporation of higher optical output power QC lasers operating at higher laser operating temperatures than our current QC laser is currently ongoing work.

Comment: 5) Comments on why the authors used an over-modulated signal to calculate the background noise would be helpful. Page 7017 (Lines: 10-29): Did the commonly used method of tuning the laser slightly to a non absorbing region or to a region with minimal or no ammonia absorption for background measurements pose limitations?

Response: We add to the revised manuscript (section 3): "The over-modulated 2f NH3 signal is used to calculate the background noise, since it minimizes the influences of residual NH3 on the 2f signal." For a modulation index of 5, the 2f NH3 signal magnitude is reduced significantly (by 67%). We add the following description at the end of section 3.3: "We note that other potential methods to achieve background measurements have limitations for our system. One approach is tuning the laser to a different

wavelength region. However, the QC laser used here has a limited tuning range and this method will produce a different baseline due to changes in laser optical power, detector response and interference fringing. In addition, there are other absorbing species (e.g. H_2O, CO_2, O_3, SO_2) that will contribute to the spectroscopic baselines on either side of the NH_3 spectral feature of interest."

Comment: 6) The 1σ detection is called the noise equivalent limit and not the minimum detection limit. Detection limit is typically defined either as 2σ or 3σ. Page 7017, last line:

Response: The terminology is changed to noise-equivalent limit to describe the 1σ detection. The minimum detection limit is defined as 2σ, in the revised manuscript. We also note in the revised manuscript (section 5), the 1σ detection is equivalent to $\sim 3 \times 10\text{-}5$ fractional absorbance, which is within a factor of 3 compared with typical detection limits for laser spectrometers.

Comment: 7) The 2f signals plotted in Fig 7 and 8 are superimposed on a non-linear background. Is this due to other nearby absorbing gases?

Response: The non-linear background is mainly due to the non-linearity of the detector response and the intensity modulation due to changes in laser optical power through the scan range used. Other effects contribute to this baseline, including interference fringes. The baseline is discussed in the revised manuscript in sections 2.2, 2.3 and section 5 and a typical baseline is shown in Fig. 7b, corresponding to the 1.0 ppbv NH_3 spectrum shown in Fig. 7a.

Comment: 8) The 2f of ammonia in Fig. 3 and Fig. 7 appear to have different tuning ranges. What are they?

Response: The 2f spectra in Fig. 3 and Fig. 7 are obtained with the same tuning range. However, these spectra appear to be different due to a difference in the central wavelength (small difference in current bias). However, the distance between the two

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ethylene troughs, indicated by the arrows in Fig. 3, are the same in Fig. 3 and Fig. 7.

Comment: 9) Fig 7: Are both peaks shown in the figure for ammonia?

Response: The original Fig. 7 shows the 2f spectrum at ambient pressure with NH3 scrubbed from the system, so there should be no NH3 peak in this spectrum. We replace the original Fig. 7 with a new spectrum, showing the 1.0 ppbv NH3 raw 2f spectrum with fitting and residuals (Fig 7a). Figure 7b now shows the base functions used in the fitting of the spectrum in Fig. 7a as follows: 2f NH3 lineshape (top), 2f ethylene lineshape (middle) and polynomial baseline (bottom). These base functions serve to illustrate the position of the 2f NH3 lineshape peak when the ethylene reference signal is present. Attached in this author comment is the revised Figure 7.

10) Figure 10: A zero –ammonia background scan for this plot would give a better representation of system noise with time.

Response: Figure 10 is not intended to illustrate the system noise with time. This figure shows on-road NH3 field measurements, with variations due to real changes in atmospheric NH3 mixing ratios. The precision and minimum detection limit analyses in sections 3.2 and 3.3 evaluate the system noise characteristics with time.

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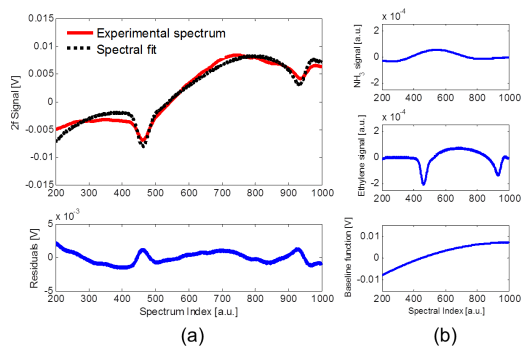
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Figure 7. (a) Second harmonic spectrum of 1.0 ppbv NH_3 signal at ambient pressure recorded at 1 Hz along with spectral fitting results and residuals. (b) Base functions used in spectral fitting in (a) as follows: 2f NH_3 lineshape (top), 2f ethylene lineshape (middle) and polynomial baseline (bottom).

Fig. 1.