

# ***Interactive comment on “Cavity ring-down spectroscopy sensor for detection of hydrogen chloride” by C. L. Hagen et al.***

**C. L. Hagen et al.**

brian.c.lee6@gmail.com

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We would like to thank all of the reviewers for their insightful comments and suggestions. Our responses are below. Given that many comments from the three reviewers overlap, we are submitting a single document as a response to all received comments. We use regular font for the reviewer's comments and bold text for our replies. We also have added a numbering system to the comments (i.e. R2.3 means the 3<sup>rd</sup> comments from Reviewer 2) since, in some cases, there are overlapping comments and replies.

Reviewer 1:

R1.1 One comment is that the manuscript is written, as if this was the first instrument using a cavity based technique in the NIR to measure HCl. However, Los Gatos Re-

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search already offers such an instrument commercially, with many of the advantages the work here mentions (telecomm, non-cryogenic, compact, etc.). I think it is important for the manuscript to:

- a. acknowledge this fact clearly (I realize it is a different cavity based technique).

**We discuss in the manuscript that there are commercial offerings, but their design and operational details are not available in the open literature. In the revised manuscript, we will add references to the Tiger Optics i-2000 HCI and Los Gatos Research HCI analyzer websites.**

- b. Compare the size, weight and power consumption of the instruments.

**The power draw, size, and weight of the above instruments are available on their respective websites. These parameters vary depending on which model is selected. Our instrument is currently a laboratory model, and is in the process of being miniaturized into a more compact field instrument. We anticipate achieving similar values to the commercial ones, with the exception of possibly the power draw. The main difference is that in order to achieve relatively fast time response (<~15 s) our system employs high cavity flow rates, and therefore high pump speeds. In contrast, the available commercial instruments have relatively slow time response (>2 min) and may not require such flow rates. (If we compare our system against off-axis type cavity enhanced systems, then the smaller volume of our cavity means we can achieve a given cavity refill time with a lower pump speed.)**

- c. If possible compare the detection limits. Unfortunately, it is likely impossible to compare the time response/cavity effects

**A short comparison will be added to the revised manuscript based on the information below:**

**The Tiger Optics i-2000 HCI reports a  $1\sigma$  sensitivity (limit of detection) of 250**

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pptv (scaled from their quoted  $3\sigma$ , 750 pptv value). The 80% response time is 2 minutes, and is presumably the integration time for the above sensitivity, though it is not explicit.

The Los Gatos Research HCl Analyzer reports a 100 sec  $1\sigma$  sensitivity of 200 pptv. The 10%-90% response time is 5 minutes.

Our instrument compares very favorably with a 1 min,  $1\sigma$  sensitivity of < 20 pptv and a 10%-90% response time of  $\sim$  15 s.

R1.2 page 7231 last paragraph: The discussion of the time response needs to be extended with more data shown.

a. steps from both zero HCl to high HCl concentration and high HCl to zero HCl concentration need to be shown

**The figure we included in the paper shows the response of the ring-down signals to a reduction in concentration. The response time (based on time needed to capture 90% of the change) was 10 s in this case. We have similar results for both increases and reductions in concentration and all yield <15 s. All measurements were for concentration changes of approximately 10 ppb with absolute concentrations in the range of 0-30 ppb. We will add text in the revised paper, and redo the Fig. 9 caption, to better detail these aspects.**

b. these need to be shown for low and high relative humidity (RH).

It was not clear to me at what RH the test was done. The reason this matters is that the wall absorption effects might have a strong and non-obvious RH effect. For example, for some setups and compounds introduction of humid air into an apparently clean system can release compounds. The step-down to zero HCl concentration is important as a critical aspect of the instrument is how long it takes until concentrations close to the detection limit can be observed after exposure to high HCl concentrations. In addition, there often is more than one time-scale and it would be interesting to inves-

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tigate this. A minor aspect is mentioning the time scale for the CIMS, which I believe was not mentioned. I strongly suggest extension of this section, which is critical for a compound such as HCl.

**We acknowledge the potentially important role of relative humidity; however, we felt that a complete characterization of inlet effects for a range of possible ambient conditions was outside the scope of this paper. We will add the following to revised manuscript: “The time response shown in Figure 9 is for dry air. It is possible that at higher relative humidity, the time response could be different due to a change in the affinity of the Teflon walls for HCl. At the low pressure and high temperature operation of this instrument (~0.1 atm, 60 C), the effective relative humidity in the cavity is 1.6% even if the sampled ambient air is 100% relative humidity at 25 C and 1 atmosphere pressure. Thus we anticipate the cavity walls will remain essentially dry even under humid conditions.”**

Minor comments:

R1.3 p. 7222, 1st paragraph: Some references for cw (sweep and switch) CRDS need to be included as it is a well-established technique.

**We will add the following references to the revised manuscript (in this paragraph):**

**Berden, G. and Engeln, R., eds.: Cavity Ring-Down Spectroscopy: Techniques and Applications, Wiley- Blackwell, 2009.**

**Gagliardi, G. and Loock, H., eds.: Cavity-Enhanced Spectroscopy and Sensing, Springer Series in Optical Sciences, 2014.**

**Lehmann, K.: Ring-down cavity spectroscopy cell using continuous wave excitation for trace species detection, 1996.**

**Romanini, D., Kachanov, A., Sadeghi, N., and Stoeckel, F.: CW cavity ring down spectroscopy, Chemical Physics Letters, 264, 316 – 322, 1997.**

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He, Y. and Orr, B.: Rapidly swept, continuous-wave cavity ringdown spectroscopy with optical heterodyne detection: single- and multi-wavelength sensing of gases, *Applied Physics B*, 75, 267–280, 2002.

Dudek, J. B., Tarsa, P. B., Velasquez, A., Wladyslawski, M., Rabinowitz, P., and Lehmann, K. K.: Trace Moisture Detection Using Continuous-Wave Cavity Ring-Down Spectroscopy, *Analytical Chemistry*, 75, 4599–4605, 2003.

R1.4 p. 7223: HITRAN simulations: were isotopes, such as HDO included?

**Yes, isotopes (including HDO) were considered. For each species considered, all the available isotopes in HITRAN were included. This will be specified in the revised text.**

R1.5 p. 7224, line 20: For an instrument description more details on the reference cell need to be added, e.g., What is the partial pressure of HCl, is there a balance gas, what is the pathlength, does the pressure have to be identical to the cell pressure and if not why, e.g., no shift in line position, or irrelevant?).

**The pressure and balance gas are already included in the manuscript: “a sealed glass vessel containing a high concentration of HCl ( $\sim 0.1\%$ ) in atmospheric pressure air.” In the revised paper we will further specify that the absorption path length is 5.7 cm. Note that the role of the reference cell is to (approximately) locate the transition line center to center the laser frequency scan. The pressure within the cell does not need to be exactly the same as the CRDS cavity, though the pressure shifts may then be different. At our conditions we estimate this difference to be  $\sim 0.01\text{ cm}^{-1}$ , while the extent of our frequency scan is  $\sim 0.08\text{ cm}^{-1}$ . Given this, and given that our fit to the CRDS spectrum includes the line center location as a free parameter, the final fit and measurements are not compromised by this shift. We will add a few clarifying sentences to the revised manuscript.**

R1.6 p. 7225, line 6-7: It would be useful for readers not so familiar with cavity en-

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hanced spectroscopy to explain why two different radii for the mirrors are used and how they relate to the cavity length.

**The two radii were chosen to achieve a stable optical resonator while roughly minimizing the needed mode-match path length (i.e. the distance between the fiber-optic output and the cavity). For example, using two 1 m ROC mirrors also gives a stable cavity, but the needed mode-match distance is longer. We will add an additional reference and clarifying sentence in the revised manuscript.**

R1.7 p. 7225 line 11, 12: Please add the wavelength of highest sensitivity of these detectors.

**Revised text will be: “Indium Gallium Arsenide (InGaAs) photodiodes are widely used for NIR detection, however, the responsivity of InGaAs diodes drops below 0.1 A/W at 1742 nm as compared to a peak of 1.1 A/W at 1550 nm.**

R1.8 p. 7225 line 29: How does digital equipment (computer) scan continuously. I assume there is a minimum step size in the current? Please give more details on how the scan is conducted.

**Revised text will be: “First the software sends an analog voltage to the laser controller scanning the laser in a triangle wave between 5739.22 and 5739.30  $\text{cm}^{-1}$  with a 1 s period (the analog output is converted from a 16-bit digital signal, which gives 520 wavelength steps over the scan range).”**

R1.9 p. 7226 line 11-15. How many individual ring downs do the 30 scans over the feature in 30 seconds correspond to. From the 25 s-1 mentioned previously I assume it should be about 750 individual ringdowns? It would be helpful to mention this number here.

**Revised text will be: “The LabVIEW software collects ring-down signals for a set amount of time (typically 30 s, ~600 individual ring downs),” Note that the acquisition rate varies from ~20 to 25 Hz from alignment to alignment. The spectrum**

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shown in Fig. 4 contains ~600 points.

R1.10 p. 7226 line 25-equation 2: For readers not so familiar with the method, it should be stated whether this is the HCl concentration in the cell or the ambient one? (dilution/ purge flow and reduced pressure in cell).

**The equation gives the ambient HCl mixing ratio and has already taken in account the reduce cell pressure and purge dilution. We will modify the text as follows: “The measured area under the spectral line, along with the cavity pressure, cavity temperature, and line strength, are used in conjunction with the ideal gas law and the Beer-Lambert law to find the ambient HCl mixing ratio.”**

R1.11 p. 7227 line 25-: Please add more details of the virtual impactor. What type of pump is used, as one of the claims made is that this instrument has low pumping requirements, and tubing diameter, length, details of the T used to split the flow.

**The following details will be added to the revised manuscript: The main system inlet is the center orifice of a 3/8" NPT PFA tee fitting. A ~1.5 mm I.D. PFA tube, leading to the detection cavity, is inserted ~5 cm into one side of the tee. The remaining side of the tee is connected to a 25 W pump (Air Supra HK-25L), which pulls 25 lpm of air through the fitting. In order to reach the detection cavity, air must enter the center tee orifice and quickly make a 180° turn into the small PFA tube. Large particles, which cannot turn quickly enough, will flow towards the impactor pump.**

**And we will add the reference: B.T. Chen, H.C. Yeh, An improved virtual impactor: Design and performance, Journal of Aerosol Science, Volume 18, Issue 2, Pages 203-214, 1987.**

R1.12 p. 7229: should the smaller length (absorption vs. cavity) be used here? Is the 11 ppt the mixing ratio in the cell as ambient would be slightly higher due to purge dilution? Please clarify.

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The reviewer is correct that using the shorter sample path length, in place of the full cavity length, will result in a slightly lower optical sensitivity and mixing ratio limit of detection. The revised manuscript will clarify this and use the sample path length here, which includes the dilution effect of the purge flow.

R1.13 p. 7232: The description of the ambient measurements needs to be extended. Relevant details such as inlet lengths, inlet material, flow rates through the inlets, individual or common inlet.

**Details of the inlet during the field study will be added to the revised manuscript. The HCI CRDS instrument used an individual inlet. The inlet was a ~1 m PTFE line heated to 60 C. The inlet flow rate was ~29 slpm (~25 slpm virtual impactor and ~4 slpm cavity flow). The time response of the inlet configuration used during the field study was not precisely measured, but was about a few minutes. (It is mentioned that this was an earlier version of the instrument.)**

R1.14 p. 7233 line 13 “somewhat”: it is a specific amount smaller, I would assume?

**Yes, though the numeric value (400 kHz) is already given in the manuscript: “First, a detector and amplifier combination with somewhat lower bandwidth (~ 400 kHz)”.**

R1.15 Figure 3: I would suggest showing the Fabry Perot Etalon instead of the reference cell and explanation of this in the caption. Define ROC in figure, please.

**The reference cell was included as this is the configuration during normal operation. The etalon simply sits in place of the reference cell. In the revised manuscript we will clarify this in the caption, and we will define radius of curvature (ROC).**

R1.16 Figure 4: Please add number of data points total shown.

**We will include this in the revised manuscript.**

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R1.17 Figure 9: see second comment for additional figures and information (RH) for this figure

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**See response to comment R1.2.**

R1.18 Figure 10: I would suggest showing binned data rather than smoothed data, which tends to take out features.

**We do not think the moving average (line) significantly distorts any trends in the raw data. We also note that the raw data, without any averaging or smoothing, is included as well.**

Reviewer 2

R2.1 P7221, L8-9: The authors should specify what is meant by 'periodic maintenance' and by the requirement of 'infrequent calibration'.

**The text will be modified as follows, "The sensor is constructed from robust, readily available, and relatively inexpensive NIR laser sources and components (similar to those used in the telecom industry), which can operate unattended for years. Due to the inherently quantifiable nature of CRDS, the only required calibration is the relative laser frequency using an etalon, as described in Section 2." See also R2.9.**

R2.2 P7221, L14: The authors mention that commercial sensors based on CRDS have become available recently. A reference to these instruments must be provided here. Even though design and operational details are not available the key specifications of the commercial instruments should be quoted here and if possible reference to same should be made later in the discussion of the instrument's performance. Ideally the instrument described in this publication should be compared to the commercial sensor. I understand, however, that this may not be a realistic expectation.

**The commercial sensors will be more fully described. See response to comment R1.1.**

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R2.3 P7221, L26-27: The authors cite Busch and Busch (1999) as well as Berden et al. (2000). Clearly by now newer books and reviews are available, e.g. book cavity ringdown spectroscopy by Berden and Engeln (2009), Wiley, or Cavity enhanced spectroscopy and sensors, Gagliardi and Loock (2014), Springer.

**More recent references will be included in the revised manuscript. See response to comment R1.3.**

R2.4 P7222, L1-10: The first paragraph represents an overview of approaches in the literature, however, no reference to any publications is made here. Appropriate citations should be included here in several places.

**More recent references will be included in the revised manuscript. See response to comment R1.3.**

R2.5 P7222, L20-25: Explanations on P- and R-branch transitions, even though meant for the benefit of the reader, should be shortened.

**We view some discussion of this topic useful for the non-specialist, but we will slightly shorten it by removing: “The transitions are labeled by the initial rotational level so, for example, R(3) corresponds to molecules changing from initial level of  $J''=3$  to final level of  $J'=4$  while P(1) corresponds to molecules changing from  $J''=1$  to  $J'=0$ .”**

R2.6 P7223, L4: “. . . much stronger line strength. . .” -> “. . . much greater line strength. . .”

**We will make the change.**

R2.7 P7223, L12-14: The authors should specify the concentration used for the simulation.

**It is specified in the figure caption, but will be added to the text.**

R2.8 P7223, L29: “. . . distributed-feedback diode laser. . .” -> “. . . distributed-

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feedback diode (DFB) laser. . .”

**We will make the change.**

R2.9 P7224, L5: What is meant by “when the system is first run,. . .”?

**Frequency calibration is run only to update the laser scan frequency calibration, which would only be done at the beginning of data acquisition, and perhaps every few months thereafter. We have not characterized the exact duration over which the calibration holds but do not see changes over several month durations. We will change “When the system is first run” to “During frequency calibration”.**

R2.10 P7224, L10: “. . .and fit to a second order polynomial,. . .” -> “. . .and a second order polynomial is fitted to it,. . .

**We will make the change.**

R2.11 P7224, L14: “these fit coefficients” -> “the calibration coefficients derived from the fit”

**We will make the change.**

R2.12 P7224, L29: “. . .causes noticeable instability. . .” -> “. . .causes noticeable instabilities. . .”

**We will make the change.**

R2.13 P7226, L8: what is meant by optically limited? Limited by the light propagation dynamics? Where does the value of 25 s come from?

**The following will be added to the revised manuscript: “Further increasing the laser scan speed, and therefore the acquisition rate, decreases the amount of light transmitted through the cavity, decreasing detector signal-to-noise ratio and reducing the overall detection sensitivity.”**

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R2.14 P7227, L15-19: This is an interesting way to determine the effective sample length inside the cavity. I had not seen this before, in case that this is a well known approach in the community.

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**No change needed.**

R2.15 P7227, L29: artifact -> artifact

**We will make the change.**

R2.16 P7228, L18: "This section discusses . . . sensor." -> "In this section . . . sensor are discussed."

**We will make the change.**

R2.17 P7229, L8: The top panel in Figure 6 shows a HCl mixing ratio. How can that be determined from zero air measurements. Is the scale on the lower panel (Alan Dev.) logarithmic? That is not obvious. Does the improvement in the variance scale with the  $\text{sqrt}(\text{time})$ ? If not, what can the authors say about systematic errors affecting the longer term performance of their instrument?

**We follow a widely used approach of determining our system's detection limit by examining the noise of our measurement baseline, which we find by purging the cavity with ultra-zero air. During the zero-air measurements, the data acquisition system was run as normal and allowed to fit the measured data. Ideally, all measured concentrations would be zero. The vertical axis is logarithmic. Due to the small range of values spanned, the plot with log and linear axes looks essentially the same. We will change to a linear axis. For reasons that are not yet clear to the authors, the first 3 data points do not follow a  $\sqrt{\text{time}}$  improvement. From times 2 to 5.5 minutes, the variance improvement follows  $1/\sqrt{\text{time}}$  with an  $R^2=0.99$ . As expected, the deviation eventually curves above  $1/\sqrt{\text{time}}$  at later times, which is inherent to all instruments.**

R2.18 P7230, L19: A reference for incoherent broadband cavity enhanced spec-

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troscopy should be included.

**The following reference will be added to the revised manuscript: Fiedler, S. E., Hese, A., and Ruth, A. A.: Incoherent broad-band cavity-enhanced absorption spectroscopy, Chemical Physics Letters, 371, 284 – 294, 2003.**

R2.19 P7232: Section 3.4 appears to be not detailed enough and too short considering the message that is to be conveyed here. Figure 10 is not discussed sufficiently. The instrumentation that CRDS is compared with is not outlined in sufficient detail. A general discussion on precision and detection limits (general specs of the other instruments) is missing. The data shown are not normalized to the same integration times. An additional figure or an additional panel in Figure 10 showing a correlation plot together with an appropriate error discussion is missing here to improve the impact of this section, in my opinion.

**In the revised manuscript we will provide additional details on the other field instruments to which our instrument is compared. However, as stated in the manuscript, our instrument was still in its developmental stages during the field study, and thus, we do not feel exhaustive comparison is warranted. The data shown is still useful to show the field worthiness of the (early) instrument.**

R2.20 P7233, L11: The statement “..is very adequate. . .” is too vague and should be better specified.

**The performance and applicability of our sensor is discussed in the conclusion section. To avoid redundancy we will simply remove the above mentioned statement from the revised manuscript.**

R2.21 P7233, L24: aircraft -> aircrafts

**We will make the change.**

R2.22 P7235, L4: The commercial instrument is mentioned again here, see comment above.

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We will modify our discussion of available commercial instruments. See comment R1.1.

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R2.23 P7241, Fig. 1: "Intensity" on the ordinate should read "line strength" or "integrated line strength". "Frequency" on the abscissa should read "Wavenumber".

We will make the change.

R2.24 P7243, Fig. 3: Include ROC = radius of curvature.

We will make the change.

R2.25 P7244, Fig. 4: What is shown on the ordinate? Unitless loss  $L/(c\tau)$  (with  $L$ =effective sample length)? The term "Optical absorption" is not particularly appropriate due to the non-zero baseline. The authors may want to refer to Eq. (1) here and mention that the "empty cavity" losses have not been subtracted, rather than referring to the "cavity mirror loss". The abscissa title should read "Wavenumber" rather than "Frequency".

We will modify the axis labels as Cavity Loss and Wavenumber ( $\text{cm}^{-1}$ ). Additionally, the caption will be updated to more clearly identify the baseline loss as empty cavity loss.

R2.26 P7246, Fig. 6: Ordinate title not clear in comparison to the text on page 7229 (see comment above). Furthermore showing data up to 200 min (half the data) in the upper panel would have been sufficient to correspond to the Allan Deviation plot in the lower panel. I also suggest citing Lehmann and Huang in the caption.

We feel plotting 400 min of data does not detract from the point being made (i.e. to show the minimum in the Allan Deviation). Additionally, the citation to Lehmann and Huang is given in the main text associated with this figure.

Reviewer 3

R3.1 P.7222: please provide one or more references to original papers where the CW-

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CRDS technique is fully explained. This is especially needed as this paper is not supposed to, and does not, offer a detailed account of the technique.

**Additional references will be included in the revised manuscript. See response to comment R1.3.**

R3.2 Same page: the essence of the CW-CRDS technique is nicely outlined in a few sentences, but there is one missing detail which is important, in particular to understand fully some comments which occur later in the manuscript. This is about how one goes to produce those passages through resonance... and actually one can choose to modulate the cavity or the laser, with different advantages and drawbacks. It seems that here the cavity length is modulated by a piezo actuator, but that should be made explicit, in the text, and in the experimental scheme. That should allow explaining how a CRDS spectrum is actually obtained, which I think is not granted when reading the present manuscript.

**There is no PZT on the cavity mirror. Cavity resonance is achieved by sweeping the laser frequency over several cavity free spectral ranges. In the revised paper, we will clarify the text as follows: “The laser is scanned over a spectral line of the analyte, which spans  $\sim$ 15 cavity free spectral ranges. As the laser frequency overlaps with a resonance of the static cavity, significant intra-cavity power is built up.”**

R3.3 P.7224, bottom: usually a fiber-pigtailed DFB laser includes an optical isolator. Please explain if this was the case of the used laser and comment on the fact that this isolator was not sufficient, and maybe how that became evident.

**We will add the following to the revised manuscript: “Although the DFB laser includes an internal isolator (20 dB per manufacturer specification), it did not sufficiently extinguish the back reflection from the cavity, causing small fluctuations in the ring-down time.”**

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R3.4 P.7225. “The bandwidth is approximately 5 times larger than needed in order to not distort the ring-down signals”. . . This does not seem to be right. The bandwidth associated with a ringdown of 170  $\mu$ s should be more like 1kHz ( $2\pi f_c = 1/\tau$ ). Also, sampling at a digitization rate close to the detector response time, provides a ring-down signal whose fit procedure takes care of averaging the noise over the seemingly excessive number of data points, resulting in the same noise level on the ring-down value as when using a slower detection/digitization chain. Thus in general there is no penalty, and one advantage is a large dynamic range since the same detection chain allows to appropriately detect and process fast ring-down decays which may appear in correspondence of a strong absorption line. On the other hand, excess noise is certainly produced by aliasing when the digitization rate is slower than the detector response time (a low-pass analogue filter should then be used to match the two).

**The choice of both detector bandwidth and digitization rate is interesting. We follow the recommendations of Lehmann and Huang (citation below) who write: “From the above considerations, it should be clear that for optimal signal processing in CRDS, one wants to select values of  $k_f$  and  $\Delta t$  such that  $k_f \Delta t \sim 1$  and  $k \Delta t \ll 1$ .” Where  $\Delta t$  is the digitization interval,  $k=1/\tau$ , and  $k_f = 2\pi \times \text{bandwidth}$ . For 170  $\mu$ s,  $k=5700$  Hz. Currently, we have  $\Delta t=0.4 \mu$ s giving  $k \Delta t = 0.002$ , and have clearly satisfied  $k \Delta t \ll 1$ . If, as we suggest, we move to a detector bandwidth of 400 kHz, we would then also satisfy  $k_f \Delta t \sim 1$ . That said, we could arguably drop the digitization rate from 2.5 MS  $s^{-1}$  to 250 kS  $s^{-1}$ , and decrease the detector bandwidth to 40 kHz (more in line with the reviewer’s suggestion), thus also satisfying the above requirements. However, as the reviewer points out, it may be useful to maintain a large dynamic range in the ring-down time constants our detection system can handle. We will add a short discussion of these aspects to the revised paper.**

**Lehmann, K. K.; Huang H. F. Optimal signal processing in cavity ring-down spectroscopy; In Frontiers of Molecular Spectroscopy; Lanne, J., editor; Elsevier:**

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R3.5 P.7226. Please explain what is limiting the ring-down acquisition rate to 25 per second. Concerning the interesting strategy of fitting Voigt profiles using a pre-calculated table of values, does that mean that the laser scan is sufficiently stable in time that a fixed grid of frequencies can be used? Or is the situation more complex, as I suspect? It may be worth to give more details on this interesting point.

**The following will be added to the revised manuscript: “Further increasing the laser scan speed, and therefore the acquisition rate, decreases the amount of light transmitted through the cavity, decreasing detector signal-to-noise ratio and reducing the overall detection sensitivity.”**

**With respect to the Voigt fitting, the following will also be added: “Interpolation is used to infer Voigt profile values for laser frequencies between the tabulated values.” (As the reviewer suspects, we cannot, of course, maintain exact pre-determined laser frequencies for our actual ring-down measurements.)**

R3.6 P.7227. The discussion about the integrated line intensity is a bit confusing... It may be clearer to make explicit reference to the Beer-Lambert law (of which the authors seem to be using the approximation for small absorptions  $\Delta I/I = -kL$ , which is completely reasonable in this context...).

**The manuscript does state the Beer-Lambert law is being used and we have indeed employed the optically thin limit. The discussion of what is being calculated by this equation will be clarified slightly in the revised manuscript, see comment R1.10.**

R3.7 Same page: Please give references about the virtual impactor system and design.

**See comment R1.11.**

R3.8 P.7229: In order to get a more quantitative feeling about sensitivity improvement afforded by CW-CRDS over multipass or other techniques, authors could mention the



(approximate) ratio of line strengths for the two HCl absorption bands being considered. Same page. The ringdown statistics at a single frequency data point do not account for the presence of fringes on the acquired spectra. Thus, these only provide an upper limit on system performance which may be quite far from real system performance. Please provide the rms noise on the spectra baseline (or in the limit of zero sample absorption).

**The fundamental transition (1-0) has about a factor of 50 greater line strength than the 2-0 band. This information will be added to the text. The ring-down times shown in Fig. 7 were obtained by scanning the laser frequency over the nominal scan range ( $0.08\text{ cm}^{-1}$  in extent) and therefore include fringe effects (that would not appear in a measurement at a single frequency).**

R3.9 P.7230. “The scanning approach captures the baseline on either side of the absorption feature (useful for reliable fitting), but at the cost of lower detection sensitivity.” Is this the only reason for a lower sensitivity, did the authors consider the presence of interference fringes in their CW-CRDS spectra?

**There may be additional sources of discrepancy between the theoretical detection limit and what is observed, of which we are not aware. However, as per the comment above, fringe effects were included in this analysis.**

R3.10 Same page, the discussion about the calibration curve seems a bit optimistic. The agreement of many data points is within 2 sigma and the deviations appear systematically in excess for low concentrations. Could that depend on memory effects and on the sequence used to obtain these measurements? Also, the dynamic range of this calibration is a bit limited, just one decade starting from 1 ppb, while the instrument is then used to measure sub-ppb concentrations. I understand it is difficult to obtain lower or higher concentration for this molecule. . . but more discussion about this point would be welcome.

**Prior to taking measurements, the HCl concentration was allowed to stabilize**



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for more than 10 minutes, which is well in excess of the system time response. We do not think memory effects played a significant role in these data. While we acknowledge the measured concentrations were large compared to the system's limit of detection, we were unable to obtain validation sources below 0.75 ppbv. (This is a challenging issue as the reviewer acknowledges.) In the revised manuscript, we will remove the comment on systematic errors not being observed and we will explain that available calibration sources limited the measurement range.

R3.11 P.7233. The comparison of signals from the instrument and other devices is quite convincing and impressive, given the very low trace HCl level. However, this comparison appears to be of rather limited duration, and one is left with the doubt that the agreement may be episodic. If possible, the authors should discuss if such good agreement could be observed in practice over longer time scales, which would confirm that the instrument is calibration free at the level of required accuracy.

**The authors agree the comparison shown is of limited duration, and may not be completely conclusive. However, no other field data is yet available. During the initial field study discussed here, the instrument was still in the developmental stage and stable operation was only achieved near the very end of the field campaign. We look forward to additional future opportunities for comparison.**

R3.12 Same page: The argument leading to a possible improvement of a factor 5 is too simplistic. The limiting factor is typically the fringes in the acquired CRD spectra, which appear at a given averaging level. Faster ringdown acquisition will allow to reach this limit sooner, but not to improve the fringe level, thus the detection limit will stay constant.

**The reviewer makes a good point and we will modify this part of the text in the revised paper accordingly. We note that, for a field instrument, it would still be very useful to achieve the same detection limit in a shorter time period (even if**

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the ultimate detection limit is not improved).

R3.13 In the conclusion section: It would be interesting to provide an outlook concerning the isotopic ratio measurement of HCl. . .

**The two most common isotopes of HCl are  $H^{35}Cl$  (75.76%) and  $H^{37}Cl$  (24.23%). The presented instrument measures the mixing ratio of  $H^{35}Cl$ . The R(4) line of  $H^{37}Cl$  can be measured with low spectral interference at  $\sim 10$  cm<sup>-1</sup> from the interrogated  $H^{35}Cl$  line and has a line strength approximately 3 times lower than  $H^{35}Cl$ . Thus, sensitive ambient measurements of the two strongest HCl isotopes should be possible. Isotopes containing deuterium are much more rare, but may be measurable under laboratory conditions using high concentrations of HCl. We will add a short discussion to the conclusion of the revised manuscript.**

R3.14 Fig.4: The units of the vertical scale are confusing. Is that the absorption per pass in the cell? It may be more general to give the absorption per cm, so one does not need to check out for the sample length. Also, it may be clearer to write  $\times 10^{-7}$  on the scale labels.

**See comment R2.25. Also, the  $10^{-7}$  will be moved to the scale label.**

R3.15 To illustrate the quality of recorded spectra it would be interesting to add a figure displaying an absorption line with a high S/N, obtained at higher concentration, together with the Voigt fit and the corresponding residuals.

**The spectrum shown is from a relatively high concentration of  $\sim 5$  ppbv (given typical ambient levels). Certainly for much higher concentrations we will see smaller residuals. (Again, given calibration source availability this is a bit tricky, but we see this when measuring stronger water lines with the same system.)**

R3.16 Fig.6: strange that the beginning of the Allan Variance is flat... any comments about that? Why the average concentration does not seem to be zero (upper plot)?

**Note the beginning of the Allan Variance represents only  $\sim 2$ -3 points, as the**



measurement time is 30 seconds. That said, the authors cannot explain why these initial points do not follow a  $1/\sqrt{\text{time}}$  improvement. See also comment R2.17. The reason for the non-zero average is also unknown at this time.

R3.17 Fig.7: To allow easier comparison, the authors should use the same time units as in the previous AV figure. It looks like this AV shows quite a shorter system stability compared to the previous figure. . . any comment about this?

**As Fig. 7 shows, the ring-down times exhibit stability for ~30 seconds, based on which, we perform 30 second acquisitions in order to record spectra to determine HCl concentrations. Figure 6 shows these concentration measurements recorded at 30 second intervals and their associated variance. Because each of these HCl concentration measurements use their own baseline ring-down times (are self-referenced), they should not be influenced by the drift in any previous measurements. Rather, some other, longer, mechanism is limiting the stability of the mixing ratio measurements.**

R3.18 Fig.10: what are the units of time, days? What does MST mean?

**The units are in hours, which will be included in the axis label. MST is the standard acronym for the Mountain Standard Time timezone (this will be clarified).**

R3.19 A couple of general comments: I agree with the other referee that the memory effects and the good correspondence of measured and generated HCl levels may depend also on the water vapour partial pressure. Tests including a variation of this factor would be interesting. It would also be interesting to know if there is any dependence of the response time (going from zero to a given concentration, and back), as a function of concentration. In particular, exposure to high HCl levels may produce a long exponential tail before the measurement is really back to zero within the instrument sensitivity of tens pptvs.

**See comment R1.2.**

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Technical corrections:

R3.20 P.7222, line 12: "...the details of which..." => ". The details of this procedure..."

**We will make the change in the revised manuscript.**

R3.21 Fig.2: using a vertical log scale would allow to easily compare weak and strong absorption lines.

**We feel using a linear scale gives a better sense of scale of the HCl feature size compared to neighboring features.**

R3.22 P.7224, line 25: "...positioned relative to the fiber beam-splitter output..."

**We will make the change in the revised manuscript.**

R3.23 Better define the flux unit (slpm) at its first occurrence.

**We will define this acronym in the revised manuscript.**

R3.24 P.7229, line 15: "...are somewhat better than those of past work..."

**We will make the change in the revised manuscript.**

R3.25 P.7233, line 10: "..., we note that the current..."

**We will make the change in the revised manuscript.**

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