Reply on RC2
Henning Finkenzeller et al.


Response to reviewer comments

We would like to express our gratitude to the reviewers for taking the time and for providing helpful comments on the manuscript. We address the comments point by point below, with reviewer comments in bold font, responses to comments in regular font, and changes to the manuscript in quotes. Additionally, we carefully re-read the manuscript, corrected typographical errors, and made minor editorial changes.

Reviewer 2 comments

Finkenzeller report two new methods for calibrating broadband optical cavities (IBBCEAS/BBCEAS/CE-DOAS). While broadband optical resonators have been used in laboratory and field measurements for over a decade, the question of how to calibrate instruments is still a challenge for researchers. Although several methods have been proposed and are useful in various contexts, they all have disadvantages, whether additional expense or the inconvenience of requiring bottled gases. The paper therefore addresses an important technical aspect of the use of broadband optical resonators.

The authors describe the considerations around calibration and propose two methods:

- a method for ringdown calibration of narrow wavelength band using narrow bandpass filters. Here, the calibration is carried out across a wide spectral range by exploiting the angle-dependence of the centre wavelength of pass band. This approach is therefore a convenient approach to carry out a conventional ringdown calibration across a wide spectral region.

- A more important development is their proposal of Integrated Calibration by means of Optical Modulation (ICOM), which uses both a modulated light source and an additional modulator to characterise the optical cavity pathlength.

ICOM in particular is a useful advance that delivers highly accurate measurements of the effective pathlength of the resonator. The authors provide
modelled and experimental results of both calibration methods and compare these to a commonly used calibration approach based on differences in Rayleigh scattering of two gases. The results of both new calibration methods are very good and agree well with the Rayleigh calibration, indicating that both methods are accurate and not too expensive.

The methods proposed here are likely to be valuable tools for researchers using optical resonators. I have a few comments and questions regarding the paper.

Several clarifications would strengthen the manuscript:

- The authors should clarify the difference between phase shift measurements (Langridge, 2008) and the approach taken here. They are not the same, but it would be instructive to describe and explain the different approaches more clearly.
  We have amended the introduction.
  “PSCRDS employs a modulated light source (typically direct modulation of an LED, pulse length a few 10 ns) and a fast detector (photomultiplier tube, PMT). Spectral information is gained with a monochromator. The temporal evolution at the selected wavelength is sampled with a phase-sensitive lock-in amplifier. The measured phase shift readily determines the intra-cavity photon lifetime. PSCRDS therefore differs from ICOM in both the hardware and the analysis approach.”

- The text (79-83) should make clear that the Rayleigh scattering approach to calibration requires two pure gases for the calibration, not just one.
  We agree that the approach relies on the comparison of two gases and have amended the paragraph accordingly. We have also made clear that zero air can in principle be used, if the contribution of O2-O2 CIA is accounted for:
  “One can determine the setup properties by comparing gases of known and distinct Rayleigh scattering coefficient, e.g. helium and zero air [Washenfelder et al 2008]. Helium scatters less than air, such that more light passes to the spectrometer. In the case of zero air, O2-O2 collision-induced absorption needs to be considered as well.”

- Use of H2O absorption is challenging for optical cavity measurements because the narrow absorption lines of gas phase H2O are unresolved by typical spectrometers, resulting in apparent non-Beer-Lambert behaviour. This should be clarified in the text.
  We appreciate the comment and have amended the paragraph accordingly:
  “For water, strong absorption in narrow absorption lines that are not resolved by typical spectrometers can lead to apparent non-Beer-Lambert behaviour, and special care may be required in the interpretation [Langridge et al 2008].”

The authors put the modulator after their resonator, but they should indicate whether this is necessary, or whether it is possible to put the modulator before the resonator. Presumably, as a product of different time-dependent transmission functions, the two arrangements are mathematically equivalent.

The optical modulator needs to be introduced into the light path between the resonator and the spectrometer. It cannot be introduced between the light source and the resonator. If introduced directly after the modulated light source, it would effectively only change the modulation of the light source, but no information on the resonator as, in this configuration, external component would be gained. We have further clarified the position of the modulator in the introductory paragraph of ICOM.

40 min is a long time for the calibration. What is the maximum phase interval that retains sufficient calibration accuracy?
We agree with the statement that 40 min can be substantial under certain circumstances, e.g., when setting up a new instrument. We agree that the optimization of the data acquisition procedure holds potential to shorten the calibration procedure.
Optimization could include the number of sampled phases, the spacing of phases (uniformly distributed or distributed according to the information density), the spectra acquisition time (both total and individual, to ensure good statistics even when the transmission is low), and sampling sequence of the different phases. Additionally, time may be saved by focusing data acquisition to relevant wavelengths only, i.e., to wavelengths with substantial path length that are later actually used for the retrieval of trace gas concentrations. To systematically explore this parameter space is beyond the scope of this study.

We are reluctant to recommend a maximum phase interval, but are willing to hypothesise based on the number of features that the apparent transmission can be assumed to be composed of. For a typical modulation with a frequency similar to the decay rate, for a variation of the phase from 0° to 360°, the transmission will vary between the four regimes of least-transmitting, ring-up-transmitting, maximally-transmitting, and ring-down-transmitting. Assuming that each of these regimes can be sampled using a small set of phases (e.g., 6 distinct phases), then the characterization of the entire apparent transmission could be achieved with, e.g., 24 phases, or 15° phase separation.

Typical CE-DOAS or ICAD instruments, e.g., ICAD NOx and HONO monitors by Airyx, regularly record reference spectra free I0(λ) of absorbers. The ability to reproduce I0(λ) is evidence for an unchanged mirror state, while a degradation of I0 indicates that a new calibration is needed. Under these circumstances, a calibration may not be indicated for many days or weeks, rendering a calibration duration of ~1 h acceptable. More rapid calibrations, e.g., when setting up a new instrument, can be achieved at the expense of signal-to-noise ratio. The total avoidance of measurement gaps is in principle possible by extending ICOM to include the retrieval of trace gas concentrations during the calibration, albeit requiring an advanced analysis algorithm.

**What is the estimated uncertainty in the Rayleigh method and the NBCRD measurements? Can the authors put a quantitative upper limit on their uncertainty for the ICOM approach (for typical mirror reflectivities)?**

The introduction of different transfer optics (in case of NBCRD) and a different gas (in case of the Rayleigh method) means that a constant optical alignment and instrument illumination between calibrations and measurements is not guaranteed. We interpret that the uncertainty of both the Rayleigh-derived and NBCRD-derived path length is not determined by a lack of precision, but rather limited by systematic uncertainties. We have amended the paragraphs as follows:

"Incomplete flushing of the resonator volume with helium can bias the path length short. Additionally, the exchange of the resonator gas-bath by helium can alter the instrument illumination, compared to the illumination during measurements. This can bias the retrieved path length long or short (compare non-physical negative path lengths at 405 nm and 495 nm wavelength, Fig. 11). While the helium calibration achieves small statistical uncertainties of a few 10 m (same order as noise on the curve), systematic errors due to incomplete flushing and drift in the light source intensity are likely much larger. Based on the derived non-physical negative path lengths, the accuracy of the helium-derived path length estimate is on the order of 300 m for the used setup, or 5% of the peak path length.

[...]

The accuracy of the NB-CRD path length estimate is comparable to the accuracy of the helium-derived path length estimate, i.e., on the order of 300 m, or 5% of the peak path length."

We appreciate that the reviewer presses for a number on the uncertainty of ICOM. While ICOM does not necessarily require the modification of the instrument illumination and is therefore likely more accurate, we are unable to provide a number with confidence.
Fig. 12: It would be more useful to see the percentage uncertainty in the pathlength rather than the absolute value since the pathlength changes enormously over the spectral range.
We agree that a relative comparison is relevant and could be complementary to the absolute comparison. At the same time, a relative comparison would suffer from division by zero at the spectral margins. We have amended the caption by the percent value for peak pathlength to convey the relative information in addition to the absolute information.

Minor corrections

There are a considerable number of errors in the writing. Some of these are indicated below, but the authors should carefully review and edit their manuscript.
We have carefully reread the manuscript, corrected typographical errors, and made minor editorial changes.

16: “along its propagation” is obscure & probably incorrect. I recommend replacing with “along its propagation path” or “as it propagates”
Changed to “along its propagation path”.

19: rephrase “factor of up to several 10”. One to two orders of magnitude?
Changed to “one to two orders of magnitude”.

23: add “or”
Changed to “It is a characteristic property of broad-band cavity enhanced absorption spectroscopy (BB-CEAS) or cavity enhanced differential optical absorption spectroscopy (CE-DOAS)”

31: “commonly reaches A few percent”. Added.

32: “determined through sole geometrical considerations.” -> “determined solely by geometrical considerations, unlike for multipass cells”
Changed as suggested.

40: “Periodic”
Corrected.

90: “As such, “
Changed.

93: “as a consistency”
Changed.

96: “do not combine high spectral and absolute accuracy”. It’s spectral coverage, not accuracy, that is the issue; “absolute” (of L or R, not wavelength) seems here to mean “very good” (as opposed to “relative accuracy”). I think the authors mean something like “high accuracy with broad spectral coverage”.
We appreciate the concern of the reviewer. Indeed, the combination of sufficient spectral coverage, resolution, and accuracy, i.e., precise and unbiased retrievals for every wavelength, is desired. We have considered the concern and reworded the paragraph for more clarity:
“While the above methods work in principle, they substantially complicate the use of optical resonators and are either difficult to implement or do not allow to accurately retrieve the path length with spectral resolution and coverage. Here, we present two new methods, (1) Integrated Calibration by means of Optical Modulation (ICOM), which allows
a high accuracy with spectral resolution and coverage in a relatively simple setup, easing the hitherto needed efforts in calibration.”

97: as for 96.
See response above.

130-3: Add reference to Fig. 3.
Added.

163: change to “were based on the instrumental setup used”
Changed to “are based on the instrumental setup used”.

171: “This approach relies on”
Corrected.

168: “fixed value”
Corrected.

Fig 8 caption: Change “depend indicate”
Corrected.

223: Start with “A look-up table”. Is k defined previously?
Sentence structure adjusted to start with “A look-up table”.
In the submitted manuscript, k was introduced in lin 223. We agree that it could be introduced more clearly, which is considered in the revised version of the manuscript, i.e., k is now introduced in the first sentence of the paragraph.

228: “As such,”
Corrected.

251: Sentence unclear.
Sentence revised to: “The measurement cell of the instrument was then purged with ambient air and helium repeatedly to verify complete flushing from reproducible intensity changes.”

261: Fig 6.1?
Reference corrected.

290: Residuals partially what? “Arise”? Unclear
Corrected.

Table 1: explain the symbol “o” in caption
Caption amended by “adequate sufficiency (o)”. 