

Interactive comment on “A broadband cavity ringdown spectrometer for in-situ measurements of atmospheric trace gases” by M. Bitter et al.

Anonymous Referee #1

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General comments:

Bitter et al. have developed a novel variant of the cavity ring-down spectroscopy method that is shown here to be very well suited to the measurement of trace atmospheric constituents with absorption spectra in the visible region. The technique relies on propagation of a broad bandwidth laser pulse within a high finesse optical cavity that is open to ambient air. The light leaking from one end of the cavity is dispersed onto a CCD array and the time dependences of different wavelength bins are analysed to extract absorption losses and thus spectra. This paper pays particular attention to technical details of the spectrometer and the data analysis, but illustrates the instrument's performance with measurements of NO₃, OIO and I₂ in the few pptv or tens of

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pptv ranges during the NAMBLEX campaign at Mace Head. Although NO₃ measurement by CRDS has been previously demonstrated by a couple of other groups (using narrow bandwidth laser methods), the application to OIO and I2 measurements is new and provides a powerful complement to more established DOAS methods by obtaining concentrations at a point, rather than averaged over a long atmospheric pathlength. Interference by water vapour absorption, via weak overtone lines, presents a particular difficulty for the broad band CRDS measurements, requiring careful subtraction of the structured absorption features with due allowance for the resolution of the spectrometer and the saturation of absorption over the long CRDS pathlengths. The manuscript provides a clear description of how this complication is overcome.

Overall, the paper is clearly written and is well illustrated, with a comprehensive list of references. It describes an elegant spectroscopic technique that has been successfully applied to measurements of atmospheric composition.

Specific questions:

There are a couple of instances in the text where reference is made to improved sensitivity (or lower detection limits) achieved by long-time averaging over periods of tens of minutes. The authors do not explain in detail how such improvements come about. Although there is common acceptance of the idea that greater averaging improves sensitivity, this will not be the case if the CRD spectrometer is not sufficiently optically stable over such long times. Small drifts in the mirror alignment caused, for example, by temperature changes, vibrations or exposure to wind will change the ring-down behaviour over the course of measurements made over minutes or longer. If the individual ring-down traces for each laser shot are co-added prior to fitting, the result will be a decay that is multi-exponential, and fits to a single exponential will introduce errors. If the ring-down decays are fitted individually, a drift in the ring-down rate with time will likely be observed. Can the authors thus explain further how they carry out these long-duration measurements?

The use of an open optical path is an interesting capability of the instrument: others using CRDS for atmospheric composition measurements have preferred closed paths and have thus had to quantify carefully the losses of radicals such as NO₃ to the walls of the air sampling lines and optical cavity. The advantage of absence of wall effects in the current instrument seems at least partially offset by the effects of aerosols (which are typically filtered in CRDS instruments with confined gas flows). Although not apparently a problem in the analysis of wavelength dispersed spectra, the aerosol extinction does have a consequence of reducing considerably the ring-down times achieved by the spectrometer (aerosol losses are greater than losses caused by imperfect mirror reflectivities). As a result of the shorter ring-down times for open path measurements, the limiting sensitivity of the method will be adversely affected. Can the authors thus say more about their choice of a cavity open to ambient air for measurements, as opposed to one in which the air is sampled through an aerosol filter and a flow tube?

In a similar vein, comparisons between the use of broad and narrow bandwidth light sources for CRDS measurements seem pertinent. The broad-band approach has the clear advantage of obtaining spectra in a single-shot manner, and thus reveals any interferences from overlapping absorption features. Spectral analysis can draw on techniques developed for DOAS measurements. It does, however, introduce the additional complexity of the need for very careful subtraction of water absorption lines, whereas the narrower bandwidth spectrometers of Brown and coworkers and Simpson and coworkers can be tuned to frequencies that avoid overlapping water lines. The broadband approach is also largely restricted to the visible region of the spectrum, whereas diode laser methods can extend into the infra-red, and narrow bandwidth pulsed lasers can be frequency doubled into the ultraviolet (although I am not aware of any field measurements of atmospheric constituents so far carried out by UV CRDS).

The description of the method of removal of the aerosol extinction is limited to mention of fitting a linear or quadratic function along with the water and NO₃, OIO or I₂ bands. How critical is it to treat this (presumably slowly varying with wavelength) aerosol sub-

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traction correctly to retrieve radical and molecular mixing ratios, and how confident are the authors that they are doing so?

A feature often observed in CRDS spectra obtained by scanning the wavelength of a narrow bandwidth laser is an oscillatory baseline that can be attributed to interference effects within the mirror substrates and coatings of a well-aligned cavity. I cannot see any evidence of such oscillations in the spectra presented in the paper. Is this a problem in the broad band CRDS technique, and, if so, how is it dealt with?

Is a lens used to couple the laser light into the optical cavity and thus promote excitation of TEM₀₀ modes? Figure 1 does not show such a lens, and there is no mention of mode matching in the text. If such a lens is not used, is any mode beating observed in the individual ring-down decays?

Table 1 lists some typical atmospheric path lengths but it is not clear how these are derived. If they are calculated from ring-down times (as $c \times \tau$) for the peak mirror reflectivities and the cavity lengths, larger values should be obtained. Do the values in table 1 make use of average mirror reflectivities, or include the effects of aerosol extinction and Rayleigh scattering?

I am not wholly convinced by the specified detection limits in the conclusions. From the spectra shown in figures 12 and 13, it is difficult to imagine that an absorption due to 1 pptv of NO₃ or 20 pptv of I₂ could be distinguished from the baseline after water absorption subtraction (for a 100 s accumulation time). Does the fit error quoted in each figure really correspond to a detection limit?

Technical corrections:

Page 3497 line 10: mirror not mirrors Page 3497 line 15: include not includes Page 3497 line 16: summarises not summaries Page 3498 line 7: NAMBLEX not NAMBIEX Page 3501 line 13: a not an Page 3516 line 21: Recipes not recipies Figure 3: legends in parts (b) and (c) for the red and green lines are missing.

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