

Interactive comment on “A cavity ring down/cavity enhanced absorption device for measurement of ambient NO₃ and N₂O₅” by G. Schuster et al.

G. Schuster et al.

Received and published: 16 October 2008

We thank this referee for his / her review. Our replies and indications of changes to be made to a revised manuscript are listed below.

Comment The paper highlights size, weight and cost of construction as major advantages but gives no real detail (for example, an overall design drawing for the instrument) to support these claims. Some further description of these aspects of the instrument would be helpful to support these statements.

Reply We mention the weight of the instrument, its power consumption and its cost. As a prototype device, many of the components (e.g. power supplies, flow controllers etc.) were not fixed within a well defined frame, but loosely organized around the cavity. The approximate physical dimensions are 90 cm x 40 cm x 40 cm, and this will be

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mentioned in a revised manuscript. Given that we have a schematic and a technical drawing already, it is not clear how an "overall" drawing would be useful.

Comment Abstract, line 6: The specification of the ring-down observation "over 200 μ s" could be misleading to the reader. The actual time constant of approximately 100 μ s should perhaps be quoted instead (I misread this myself on the first reading).

Reply Agreed. The reference to 200 micro seconds will be removed and replaced with the actual time constant.

Comment Page 68, line 17: N₂O₅ undergoes heterogeneous reactions, but does not affect the partitioning of NO_y (meaning here soluble nitrate ?) between particle and gas phase. The latter depends on thermodynamics.

Reply The scavenging of a gas phase NO_y species to an aerosol surface in an irreversible process impacts directly on the partitioning of NO_y between gas and particulate phases. An example is the reaction of N₂O₅ with mineral dust, which converts gas phase N₂O₅ to particle bound HNO₃.

Comment Page 69, line 13: The characterization of most available instruments is seemingly somewhat inaccurate; while the paper argues that the instrument described here offers advantages in cost and weight, other instruments to which it might be compared have been proven on various research platforms, contrary to the statement in the paper. Since the current description has not yet been designed for such research platforms, the comparison is at best premature.

Reply This statement was perhaps too vague and will be omitted in a revised manuscript. We shall however included a table of detection limits of present generation cavity based instruments (see comment by J. Orphal).

Comment Page 69, line 18: Ratio of N₂O₅ to NO₃ is more variable than an approximate factor of 10; it can be smaller than NO₃ or 1000 x larger in cold conditions.

Reply Agreed. Citing a factor for N₂O₅ to NO₃ is not really useful. We shall simply

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state that, depending on air mass, NO₃ concentrations may exceed 100 ppt, and N₂O₅ may exceed 1 ppb.

Comment Page 73, line 6: The NO₃ absorption spectrum does not undergo broadening at higher temperatures, although the peak cross section of the 662 nm band decreases. It is a curiosity of this spectrum that the width of the electronic transition stays constant while the overall intensity changes.

Reply True. There are temperature induced changes in shape between 400 and 700 nm but not within the absorption band of interest at 662 nm. We now state that the value of sigma (at circa 662 nm) changes from from 2.21e-17 at 22 °C to 1.65e-17 cm² molecule⁻¹ at 95 °C.

Comment Page 73, equation 1: Worth defining k_{rd} explicitly at this point. The "ring down decay constant" is a first-order rate coefficient the way this equation is written.

Reply OK. We now state that k_{rd} is the ring-down constant (a first-order rate coefficient with units of s⁻¹).

Comment Page 74, equation 2: In CEAS mode, other optical losses aside from mirror reflectivity, such as Rayleigh scattering and absorption from trace gases other than NO₃, should play a role. Are these losses assumed to be included in the optical path length determination, given as $d/(1-R)$?

Reply Yes, as the optical path determination is carried out with the same cell content (pressure and absorbing gasses such as H₂O) but during titration of NO₃. The path-length derived from the ring-down times is thus an effective one, suitable for application to the CEAS data if pressure etc. are the same.

Comment Page 76, line 14: The S/N in CEAS mode of 1 pptv NO₃ equivalent in 0.2 s demonstrates the potential of this method. However, the comparison to pulsed CRDS should quote the more recent publication, W. P. Dubé, Rev. Sci. Instrum., 77, 034101 (2006), which gives an L.O.D. of 0.2 pptv in 1s for NO₃ for comparable conditions to

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those cited here.

Reply We shall amend this and cite that the LOD achieved in CEAS is comparable to the best pulsed CRDS instruments and cite Dubé et al. The fact remains that, in terms of LOD, most other NO₃ devices do not get close to the instrument described by Dubé et al.

Comment Page 78, equation 4: The expression given for the sticking coefficient is the observed first order loss rate divided by the collision rate with the walls. However, diffusion should limit the wall collision rate at atmospheric pressure for a 0.75 cm radius tube. The authors should explicitly take this into account or else state the rate of diffusion relative to gas-kinetic wall collision rate. If diffusion is important, there could be additional uncertainty in the NO₃ transmission measurements since sample air near the walls will be more depleted in NO₃ relative to the center of the flow.

Reply For reasons described in the text related to different tubing diameters etc, the uptake coefficient is only approximate. The loss rate is too low (and thus gradients at the wall too small) to warrant a rigorous correction for diffusion limited uptake to the wall. Using the well known corrective procedure by Brown (Brown, R.L.: Tubular flow reactors with first-order kinetics, J. Res. Nat. Bur. Standards, 83, 1-8, 1978.) and a diffusion coefficient of 0.15 cm² /s for NO₃ at close to 1 atmospheric pressure, the correction to k_{obs} (and thus gamma) is less than 10 percent. This will be mentioned in the revised manuscript.

Comment Page 80, section 3.2: Filter loss measurements of NO₃ and N₂O₅ in synthetic air samples are given. Is it possible to given an estimate for the transmission of filters when sampling in ambient air containing aerosol? How frequently do the filters need to be changed in this instrument?

Reply We do not have any quantitative information on this. As we report, significant loss of NO₃ on aged filters was observed during the SAPHIR inter-comparison. A recent evaluation of filter losses using identical filters to those deployed here suggests

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that, under most ambient conditions, an hourly filter change is sufficient (Fuchs, H., Dubé, W.P., Ciciora, S.J., and Brown, S.S.: Determination of inlet transmission and conversion efficiencies for in situ measurements of the nocturnal nitrogen oxides, NO₃, N₂O₅ and NO₂ via pulsed cavity ring-down spectroscopy, *Anal. Chem.*, 80, 6010–6017, 2008). We shall mention this in the revised manuscript.

Comment Page 82–83, section 3.4: The section on detection limit and total uncertainty is focused mainly on detection limit. The uncertainty appears to be taken as being entirely due to the losses of NO₃ and N₂O₅ on inlets and filters. However, there are uncertainties in absorption cross sections and in mixing between mirror purge flows and sample flows that are not accounted for here. An accounting of all potential uncertainties should appear in this section.

Reply The information is actually contained in Table 3, where the uncertainty associated with each of the above is addressed. Table 3 is cited in section 3.4.

Comment Page 85, line 11: The described detection of a shift in the N₂O₅/NO₃ equilibrium toward N₂O₅ is not apparent in the figure, which shows only N₂O₅ measurements.

Reply Perhaps this is poorly phrased. At NO₂ mixing ratios between 10 and 20 ppb and temperatures close to 7 °C most NO₃ will be tied up as N₂O₅ if the NO₂ / NO₃ / N₂O₅ system is close to equilibrium. We now write: Relatively high [NO₂] (10–30 ppb) and O₃ at 10–20 ppb resulted in large rates of NO₃ production, whereas high [NO₂] and temperatures close to 6–8 °C favour the conversion of NO₃ to N₂O₅, so that N₂O₅ would be dominant.

Comment Page 85, description of ambient data: The NO measurements taken 5 km away indicate the likelihood of NO in the sampled air masses but cannot be used to interpret the observed variation in the data since it not likely that NO can be transported that distance at night unless O₃ is absent. NO, NO₂ and O₃ data should be described only in an average sense for the N₂O₅ data presented.

Reply Agreed. Our intention was not to use the increase in NO at the local measurement site to provide the only explanation for the steady reduction in N₂O₅ we observed after 2am. In revision, we shall merely state that the reduction in N₂O₅ was accompanied by the observed changes in NO and O₃, indicating that increases in local NO were potentially responsible for the removal of NO₃.

Interactive comment on Atmos. Meas. Tech. Discuss., 1, 67, 2008.

AMTD

1, S21–S26, 2008

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