

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

Anonymous Referee #1

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General comments:

This paper describes a new, prototype instrument for the detection of NO₃ and N₂O₅ by optical absorption using a 662 nm diode laser and either cavity ring-down spectroscopy (CRD) or cavity enhanced absorption spectroscopy (CEAS). The description shows clearly that the design is capable of detection of these compounds at levels at or below 2 pptv in a short time integration (5s), such that it can be used for atmospheric sampling of these compounds. The paper also describes sampling NO₃ and N₂O₅ and the resulting uncertainty from losses on these compounds on inlet walls and on the inlet filter. Validation of the instrument is shown for data from an environmental simulation chamber (though comparisons against other NO₃ and N₂O₅ instruments is to appear in a future publication) and an example measurement from ambient air is

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also shown.

The description does follow to some extent on recent descriptions of similar instruments from other laboratories, particularly in the aspects related to conversion of N₂O₅ to NO₃, measurements of wall loss rates and filter transmissions, and zeroing of NO₃ and N₂O₅ by NO titration. However, description of all these aspects is necessary here for a comprehensive description of the current instrument. Furthermore, the paper describes an important step in the general trend of these optically based instruments toward smaller, lighter and more versatile light sources such as diode lasers. In particular, the use of different methods for data reduction here (CRDS and CEAS) makes this paper a new and valuable contribution. I recommend publication following consideration of the comments listed below.

Specific comments:

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.

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

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.

Page 69, line 13: The characterization of most available instruments is seemingly a somewhat inaccurate; while the paper argues that the instrument described here offers advantages in cost and weight, other instruments to which is might be compared have been proven on various research platforms, contrary to the statement

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in the paper. Since the current description has not yet been designed for such research platforms, the comparison is at best premature.

Page 69, line 18: Ratio of N_2O_5 to NO_3 is more variable than an approximate factor of 10; it can be smaller than NO_3 or 1000 x larger in cold conditions.

Page 73, line 6: The NO_3 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.

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

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 NO_3 , should play a role. Are these losses assumed to be included in the optical path length determination, given as $d/(1-R)$?

Page 76, line 14: The S/N in CEAS mode of 1 pptv NO_3 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 (2%) for NO_3 for comparable conditions to those cited here.

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 NO_3 transmission measurements since sample air near the walls

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will be more depleted in NO₃ relative to the center of the flow.

Page 80, section 3.2: Filter loss measurements of NO₃ and N₂O₅ in synthetic air samples are given. Is it possible to give 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?

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.

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.

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 is 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.

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

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