Atmos. Chem. Phys. Discuss., 8, S6060–S6068, 2008
www.atmos-chem-phys-discuss.net/8/S6060/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Using a high finesse optical resonator to provide a long light path for differential optical absorption spectroscopy: CE-DOAS" *by* J. Meinen et al.

J. Meinen et al.

Received and published: 18 August 2008

1 Referee #1

We greatly appreciate the work of referee #1 on the paper we proposed. His comments will help us to make the paper more compact and readable und thus will put it in even better context for the atmospheric community.

Referee #1 point 1:

a) There certainty is one paragraph which can be straightened somewhat. We will reorganize the topic of light path reduction by combining the paragraphs p.10679, lines 1-6 and p.10681, line 26. Otherwise we were not able to find "a lot of repetition" elsewhere

in the manuscript.

b) It might surprise the referee, but indeed there is still much to learn about NO_3 since its discovery in the troposphere by Platt et al. 1980 and Noxon et al. 1980 almost three decades before. For instance heterogeneous reactions of N_2O_5 [Brown et al. 2006] influence the atmospheric lifetime of NO_3, also NO_3 was shown to show strong gradients close to the ground [e.g. Geyer and Stutz 2004, Brown et al. 2007], moreover NO_3 has been found to play a role in nighttime HO_x radical formation [e.g. Platt 1990]. We will add a few sentences briefly stating this to the introduction.

c) The usability of cavity enhanced techniques is linked to the availability of appropriate mirrors and light sources, of course. Since the coating techniques became state of the art technology in the past years there is virtually no limitation by the availability of mirrors. The need for an appropriate light source has to be considered in more detail but the market is rapidly emerging. So, every species which was detected by DOAS is a promising candidate to be considered for CE-DOAS.

To our knowledge there is a nearly continuous availability of LED light sources from 245 - 700 nm. Only a small fraction of them are availably with very high surface luminosity, but since very long light paths are not needed in every case the available light sources are probably sufficient.

Since the bromine-explosion is an interesting field of research, we propose a three color CE-DOAS setup to simultaneously measure IO, OIO and BrO in a single measurement. We plan to build a triplex resonator with 340, 445 and 545 nm and to modify our fitting routine in a way, that it includes all three spectra in one fit. The expended detection limit is in the range of the NO_3 detection limit reported in this manuscript.

We will add a short comment and a new Figure on that into the conclusion.

Referee #1 point 2:

The data analysis in this paper very much relies on equation (11) which we introduced

ACPD

8, S6060–S6068, 2008

without detailed discussion. The referee suggests to include some more details on the derivation of this formula. This is an issue we considered very faithful before writing this paper. We decided to distinguish between instrumental issues in this paper and theoretical concerns of the data analysis in a separate publication. For our point of view this is more convenient for the reader since a combined paper would have been a very long text and certainly a difficult task to read. In separating the theory from the experiment, we can discuss the theory in a more general way, which makes it easier to understand.

After repeated discussion of that issue we decided to stick on our prior decision.

Referee #1 point 3:

The referee suggested some good literature references to use instead of the reference to the forthcoming DOAS book of Platt und Stutz. We do agree with him, that published references should be used whenever possible. The DOAS book was released in 08/2008 and thus is one of the most recent publication on that issue when this manuscript will be published in ACP.

We will change the footnote on page 10669 to a normal reference in the final manuscript.

2 Referee #2

We also greatly appreciate the work of referee #2. His critical comments helped us to focus more detailed on the issues the community in interested in.

Referee #2 point 1:

The referee mentions, that there are already established techniques for the detection of NO_3 beyond broadband CEA techniques. The multi resonator approach by Dube

ACPD

8, S6060–S6068, 2008

et al. (2006) which has a very good detection limit and time resolution is emphasized especially by the referee. This technique relies on titration and thermal dissociation of NO_3 to N_2O_5 and therefore works great for the detection of NO_3. The drawback of this approach is that it is not usable for most of the other interesting trace gases. In our manuscript, we tried to point out that the aim on NO_3 is a first trial to demonstrate our device. Certainly the power of our approach is the usability of virtually any trace gas and not the displacement of existing NO_3 measuring techniques. Additionally, please see answer to referee #1, point 1.

It is commonly accepted that DOAS approaches have an "immunity" to background aerosol since their extinction varies slowly with wavelength unlike the characteristic absorption band of most trace gases (Eq. 6). So the differential absorption structure of the molecules to be measured is not affected by aerosol extinction. It is of course true that aerosol extinction does reduce the light path and thus the detection limit. However, in the experimental section we concentrate on experiments without the influence of aerosol since an additional extinction would have an effect on the effective path length of the instrument so that additional corrections are necessary. These corrections are implemented in our evaluation method and we will discuss these issues in the forthcoming "theory paper". We clearly stated this issue on page 10683, lines 4-7.

We will give a short comment on that on p.10670, line 7.

Referee #2 point 2:

Please refer to our answer 2 of referee #1.

Referee #2 point 3:

We like to thank the referee for pointing out for unclear figures of detection limits and time resolutions. We went through our manuscript in order to clarify these passages:

p 10673, line 25: The acquisition rate was approximately 1 min^{-1}.

p 10680, line 23: Again, the acquisition rate was 1 min^{-1}.

ACPD

8, S6060–S6068, 2008

Interactive Comment

p 10681, line 12-13: The uncertainty given here is the 1σ statistical error.

p10681, line 23: The temporal resolution was given by 5 x 60s for data readout from the CCD plus some seconds for data handling. Therefore the temporal resolution is about 6 minutes.

p 10681, line 26-27: The evaluation of the data yields a 2σ accuracy, which is represented by two times the fit error (1σ).

p 10684, line 20-23: The total exposure time was 5 x 60s (total acquisition time is 300s). The 1σ statistical uncertainty was $\pm$6.3pptv.

Figure 7: dotted line: The dotted line represents the 2σ accuracy of the individual fit result.

Referee #2 “smaller changes”:

We made all small changes suggested by the referee unless detailed unless detailed below.

p 10667, lines 13-19: Eq. 1 and Eq. 2 are connected by the concept of the average light path; see p. 10667, lines 7-8. Except for a clarification of absorptivity α, no change was made.

p 10669, lines 9-13 and p 10674, line 20 and p 10678 bottom: We accurately defined what we are using the term “light path” and “effective light path” for; please find the definition of L_0 on p. 10667, lines 5-8 (it is the average light path over all photons in an evacuated cavity) and the definition of L_{eff} on p. 10678, lines 17-19 (it is the average light path over all photons in a cavity with an additional attenuator).

p 10671, lines 4: A comment on the use of diode lasers and the corresponding problem with coherence will be added in this paragraph.

p 10674, line 22: This paragraph describes the experiments done and thus there was no need of purging the cavity in the field. However, we have done experiments with a

ACPD

8, S6060–S6068, 2008

Interactive Comment

purging hood. The results are published in (Thieser, J.: Cavity Enhanced DOAS: Geräteentwicklung und in-situ Feldmessungen von NO_3., Thesis, University of Heidelberg, Germany, 192 pp, 2008) and will be the scope of a future publication in a scientific magazine.

p 10675, bottom and p 10676 top: Thanks for mentioning this non understandable paragraph. We overlooked this paragraph in order to fulfill the remarks on clarity.

p 10679, line 16 and p 10680, line 3: This is certainly not a good written paragraph since we did not include the uncertainty of the quoted concentrations. The first ozone concentration in line 16 of page 10679 was estimated from the datasheet of the manufacturer. Since the device was designed for the use in aquaria and not for scientific means, the quoted production rate likely has an uncertainty of about 30% ($\sim$ 350 $\pm$ 100 ppmv). The ozone concentration in line 3 of page 10680 was achieved by the fit shown in Fig. 4. Since the wavelength range of the fit (650 – 675 nm) was rather small in comparison to the structure of ozone, the uncertainty is high. The 2σ fit error was (590 $\pm$ 200 ppmv) in this case. We will add this information into this paragraph.

p 10680, line 6: Fig. 4 shows the region used for the fit. There is no sufficient absorption of NO_2 in this wavelength range, so we did not fit it. Note, that Fig. 3 has a wider wavelength range.

p 10681, middle page: As commented before, ozone has not a sufficient absorption structure in shown wavelength interval of Fig. 6 at ambient concentrations to be quantified accurately in a mixture of absorbers. This is exactly what the “subsequent sentence” in line 15, p. 10681 expresses. However, in special application, where the ozone concentration is in the rage of tens of ppmv in the absence of other absorbers (i.e. smog chambers) a quantification of ozone is possible. The achieved value of the ozone concentration is (7.54 $\pm$ 0.82) ppmv and thus in the same order of magnitude like the value measured by the reference multi reflection cell –DOAS which measured approximately 1.5 ppmv. We will add a short comment on that into the associated

ACPD

8, S6060–S6068, 2008

paragraph.

p 10684, line 10: Please refer to our answer 1 of referee #2.

p 10690, Fig 3: The NO_2 concentration comes from a fit to the data of Fig. 3 which is not shown in this manuscript. This fit is comparable to the fit of Fig. 4 except that the wavelength range goes from 630 to 690nm. We will add a comment on that into the associated paragraph. The last sentence will be deleted.

p 10691, Fig 4 caption: The grey line is the residual as mentioned in the figure caption. There was no polynomial used in the fit and thus there is no co-variation possible. We will clarify this issue in the figure caption and the associated paragraph.

p 10693, Fig 5 caption: The NO_2 spectrum will be convoluted in the final version of the manuscript.

3 Dean Venables

Additionally to the work of the referees, we greatly appreciate the work of Dean Venables. The discussion with him is going to turn to be very useful for the upcoming publication on the theory. We can give some notes on his contribution, already.

D. Venables has mentioned regarding the concept of an optical path length that different photons travel different distances in an optical cavity. Our concept accounts for this issue by defining L_0 as an average light path over all photons inside the resonator. We will give mathematical proof for this concept in the "theory paper". The same has to be said to his concerns according the wavelength dependence of the mirror reflectivity. As we pointed out before in this contribution, there is no aerosol extinction in the measurements shown. However, we will show how to correct for broadband extinction in the forthcoming "theory paper".

ACPD

8, S6060–S6068, 2008

D. Venebles suggests using the mirror reflectivity and distance for the definition of the resonator in spite of the (effective) path length. Since our scope is to join the relatively new concept of broadband CEAS with the well-established DOAS approach, the use of an optical path length is indispensable. There are certainly different ways of evaluating broadband CEAS data which are all linked together by derivatives of Eq. 10. But since there is a large community using DOAS fitting software very successful, we decided to give them a tool to stick on their known systems. For the same reason we decided to use the acronym CE-DOAS.

After all, the lifetime of a photon in a cavity multiplied by the essentially constant speed of light gives the path length of the photon in the resonator. We see no particular reason of adopting the view of D. Venables.

4 General Author Comments

Parallel to the discussion in ACPD the data analysis of the NO_3/N_2O_5 intercomparison campaign at the SAPHIR chamber proceeded and created some new insights. It turns out that the intercomparison between the devices has to be discussed in greater detail as it is done in this manuscript. The results of our CE-DOAS device did not change and are still valid and in very good agreement to the reference multi reflection cell - DOAS device. In order to not forestall the detailed discussion of the performance of the different instruments, which is needed for the complete understanding of the experiments done at this campaign, we decided to delete Fig. 8. We will limit ourselves to the description of the performance in the text. On the other hand we will add the information of photolysis times in Fig. 7 and a more detailed description of the experiment in the text in order to give the reader a more complete understanding of the monitored process.

A detailed intercomparison of the devices will be presented in a forthcoming publica-

ACPD

8, S6060–S6068, 2008

tion.

References

Brown, S. S., Dube, W. P., Osthoff, H. D., Wolfe, D. E., Angevine, W. M., and Ravishankara, A. R.: High resolution vertical distributions of NO3 and N2O5 through the nocturnal boundary layer, Atmos. Chem. Phys., 7, 139-149, 2007.

Brown, S.S., Ryerson, T.B., Wollny, A.G., Brock, C.A., Peltier, R., Sullivan, A.P., Weber, R.J., Dube', W.P., Trainer, W.P., Meagher, J.F., Fehsenfeld, F.C. and Ravishankara, A.R.: Variability in Nocturnal Nitrogen Oxide Processing and Its Role in Regional Air Quality, Science, 311, 67-70, 2006.

Geyer, A., and Stutz, J.: Vertical profiles of NO3, N2O5, O3, and NOx in the nocturnal boundary layer: 2. Model studies on the altitude dependence of composition and chemistry, J. Geophys. Res., 109, D12307, doi:10.1029/2003JD004211, 2004.

Noxon, J. F., Norton, R. B. and Marovich, E.: NO3 in the troposphere, Geophys. Res. Lett., 7, 125-128, 1980.

Platt, U. and Stutz, J.: Differential Optical Absorption Spectroscopy - Principles and Applications, Series: Physics of Earth and Space Environments, Springer, Berlin, Germany, 597 p., 2008.

Platt, U., LeBras, G., Poulet, G., Burrows, J.P., and Moortgat, G.: Peroxy radicals from nighttime reaction of NO3 with organic compounds, Nature, 348, 147-149, 1990.

Platt, U., Perner, D., Harris, G.W., Winer, A.M., and Pitts, J.N.: Detection of NO3 in the polluted troposphere by differential optical absorption, Geophys. Res. Lett., 7, 89-92, 1980.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 10665, 2008.