The authors' answers to interactive comments on "Caution with Spectroscopic NO2 Reference Cells (Cuvettes)" by Ulrich Platt and Jonas Kuhn

First of all we like to thank the anonymous reviewer for the constructive and helpful comments. We substantially revised our manuscript in the light of these comments and we are confident that we addressed all points, which were raised. We trust that our manuscript is significantly improved now and will be ready for publication in AMT. We also thank the reviewers in the acknowledgement.
In the following we reproduce the reviewers' comments in red and add our answers (plus in most cases description of changes to the manuscript) in black.

Anonymous Referee #1

This manuscript describes the limitations of the use of NO2 cuvettes for quantitative measurements. In the draft, the impacts of chemical processes occur in a NO2 cuvette are assessed via analytical calculations alongside box model simulations. Generally, the manuscript is well written and presents an interesting topic. I recommend a publication after the authors need to address the following questions/comments.

Comments:

1. Line 40-43 (page 1): The bullet points should follow the sequence of the draft.

Response: We re-ordered the bullet points.

2. Line 12-20 (page 1): Why the case related to NO2 is preferred? The selection needs some motivation.
Response: We modified the first sentence of the 2nd paragraph of the abstract and inserted a motivating sentence. It now reads: 'Since NO2 is a particularly popular molecule to be studied by spectroscopic measurement techniques in the atmosphere (e.g. DOAS) and at the same time can be unstable in cells we chose it as an example to demonstrate that the effective CD seen by the instrument can deviate greatly (by orders of magnitude) from expected values.'

3. Lines 11-16 (page 2): The use of anti-reflective coatings for windows of a cell is very common. What will happen in the case of coated surfaces?
Response: We doubt somewhat that the use of anti-reflective coatings for windows of cells used for verification of DOAS instruments is very common. Nevertheless, this would be an approach to reduce the described effect of multiple passes. The consequence of reduced reflection can be readily calculated from the equation in the text following Eq. (1) by inserting smaller numbers for R. For instance assuming R=0.01 instead of 0.04 would reduce the fraction of radiation passing the cell three times to about 0.04%.
We added the comment '(this effect could be reduced by adding anti-reflective coatings to the cell windows)' after the sentence ending with 'three times'.

4. Line 29 (page 3): The statement “NO2 is a quite reactive gas” needs a justification (How?) or a reference.

Response: The bulk of the manuscript deals with the many reactions of NO2, so it must be quite reactive. We, nevertheless, add the phrase ‘(see rest of the section)’ to the revised version of the manuscript in order to make it clear why we come to this conclusion.

5. Line 33 (page 3): I think the use of terminology should be ‘accuracy’ instead of ‘precision’. Since the contributions from further reactions will also be a part of accuracy.

Response: We agree with the reviewer and changed the term accordingly.

6. Line 9 (page 4): To validate the statement “However, this is a slow process”, the reaction rate coefficient is required.

Response: We agree, the reaction rate is given in Table 1 (Reaction No. 2). Of course the process is mainly slow because the concentration of O-atoms is very low ($<10^9$ cm^{-3}, see Figure 6).
We, therefore, added the value of the reaction rate constant to the revised version of the manuscript and added a comment to this effect: ‘… because the O-atom concentration will be very low (see Figures 4 to 8)’

7. Line 22 (page 4): ‘k6’ unit is missing.

Response: We apologize for this omission and added the units (cm^{6}molec^{-2}s^{-1}).

8. Lines 7-40 (page 5): What will be the impact/importance of the reaction ‘R5’ on the NO2 concentration?

Response: Due to the low O-atom concentration (see above) the impact of R5 will usually be very minor. The only exception is a scenario when no O2 is added to the cell and the NOx level is very low.

9. Line 11 (page 11): How is it possible only for traces of water (but no other trace gases) to enter the cell? I think this line should be modified.

Response: Water is (1) by far the most abundant trace gas (mixing ratios around 1% in ambient air), also water is always attached to the walls of a cell (typically one to several layers of H2O). Thus it is clear that H2O usually will be the most likely contamination.
We modified the sentence (as suggested by the reviewer) to read: ’Since water is by far the most abundant (typical mixing ratios around 1%) reactive trace gas in the ambient atmosphere (not counting noble gases, CO2, H2, or N2O) it may be possible

that traces of water enter the cell when it is filled, then a series of additional reactions may play a role:'

10. Line 21 (page 11): The value of 'k20' is missing.

Response: We apologize for this omission and added the value of k20 (note that the value is listed in Table 1).

11. Line 31 (page 11): The assumption "all H2O is ultimately converted to HNO3" needs a reference.

Response: This is not an assumption but the consequence of the reaction mechanism in the cell. Nitric acid is formed from NOx plus H2O (R19, R23) and since the amount of NOx by far exceeds the amount of H2O the reaction will ultimately consume all the H2O. This can also be seen in Figures 4-8.
See also answer to Stefan Persijn, point 3).

12. Line 35 (page 11): What is and why 'laboratory air'? Why not oxygen or synthetic air? I think lines 34-37 need a realistic starting assumption.

Response: After a cell is filled with NO2 at low pressure an obvious idea is to just open the valve and let ambient air (usually laboratory air) rush in. Thus, air with the typical humidity of ambient air (e.g. 70% at 25 degrees Celsius as stated in line 35) will enter the cell. Clearly, it is important to keep the amount of water in the cell to a minimum. Dry synthetic air, or better, dry oxygen are preferred as stated in section 5.2.
To make this clearer we changed the text in the revised version to read: '… is topped with ambient (e.g. laboratory) air (which is of course not recommended, see section 5.2) …'

13. Page 12: A separate column in 'Table 1' for references (instead of the superscript in column 1) will ease the reading process.

Response: We agree in principle, however adding a separate column to Table 1 would make the table too wide for vertical display. Therefore we prefer to leave Table 1 as it is.

14. Page 14-15-16: The sub-panels of Fig. 4, Fig. 5, Fig. 6, and Fig. 7 should be labelled with the relevant pressure values. In Fig. 5, the scale for N2O4 (the top right and left panel) should be separate. For example, it can be done by plotting a separate y-axis (only for N2O4) on the right side.

Response: This is a good idea, since we split Fig. 6 into new Figures 4-8 (as suggested by reviewer #2) we added the values for the initial NO2 partial pressure in the individual figure captions. In Fig. 5 (now Figure 11 in appendix 2) we plotted [N2O4]*10 in the first two plots (for [NO2]0 = 1, 10 hPa).

15. Line 4 (Page 17): Duplicate pressure value needs to be removed.

Response: We apologize for this error and changed the caption of Figure 6 (now split up into Figures 4-8 as suggested by reviewer #2).

16. Line 5-6 (Page 17): The statement ‘initial O2 was assumed’ contradicts ‘Line 22 (Page 17) and Line 1 (Page 18)’. Which one is true?

Response: We can not find a contradiction here, in line 5 (page 17 of the initial version) we state ‘Except for the top panel initial O2 was assumed.’ while line 22 reads ‘In the top panel no initial O2 was assumed …’.

17. Line 2-5 (Page 18): The statement “there are no fundamental differences in the NO2 time series between the simple model and the full model” is not understandable (what is referred?). A table, for the final NO2 concentration at a fixed time interval (@ 300 s), would be helpful to summarize the comparison (simple vs full model).

Response: We find that the statement in lines 2-5 of page 18 is quite straightforward. Nevertheless, we added Table 2 comparing the NO2 concentrations at 1000 seconds for the various model runs.

18. Line 29 (Page 18): The wavelength for the photolysis (threshold) of NO2 to NO conversion is required.

Response: The NO2 photodissociation threshold wavelength is 398 nm (e.g. Johnston and Graham, 1974, Burkholder et al., 2015), the quantum yield for photolysis sharply drops above this threshold but is reaches zero only at about 430 nm, probably since vibrational excitation of the NO2 molecule supplies the energy deficit at wavelengths exceeding 398nm (See e.g. Mérienne et al., J Atmos Chem (1995) 20: 281. https://doi.org/10.1007/BF00694498). This is already stated in the text following Reaction 1 near the bottom of page 3 (original manuscript).
So no change to the manuscript is required here, we just used the opportunity to slightly change these numbers to the more exact values 398nm (threshold) and 430nm (quantum yield virtually zero at this and any longer wavelength), respectively in the revised version of the manuscript.