

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 comprehensive, 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 #2

In this submission, Platt and Kuhn describe how optics and chemistry alter the effect of reference cells, particularly the NO₂ reference cell. Such cells are commonly used in DOAS and gas correlation spectroscopy for wavelength calibration and absolute calibration of column densities. Although the authors show that the influence of optical factors can be appreciable, the most important outcome of this work is that it draws attentions to the complexity of the chemical composition in the reference cell when exposed to light. Changes in chemical composition can be very large indeed, and inattention to these effects will compromise measurements.

The underlying reactions are well-known and relatively easily modelled and this work presents nothing new in this respect. From the practical point of view, such factors may not be widely appreciated. Therefore, from the instrument operator's perspective, the authors offer a cautionary information about such cells, as well as practical suggestions to improve the stability of the chemical composition in these cells. The use of such cells and their influence on standard trace gas measurements by a widely used technique could make this work a valuable practical contribution to the literature.

Response: We like to thank the reviewer for this positive assessment of our work.

However, there are several aspects of this work that should be clarified and improved before publication can be recommended.

I found the manuscript unnecessarily convoluted and hard to read. A direct presentation of the calculations and simulation results would be clearer to the reader. In particular, the approach of gradually ramping up the complexity of the underlying reactions and analytical approximations seems unhelpful to this reviewer. Why not just present the full simulations? Limiting conditions could be examined separately.

Response: We agree with the reviewer that the manuscript may appear somewhat lengthy to readers who are already familiar with the details of the NO₂ reaction system. However, we feel that it is important to explain the salient points to readers, who are less familiar with the chemical aspects of NO₂ cells step by step.

1. Introduction

- The introduction is unusually short. The authors should explain how these reference cells are used in terms of calibration and column density, how this could lead to errors, and what sort of errors could arise. Would errors be expected for the wavelength calibration, for instance, even if the NO₂ concentration in the cell changes? More equations in this part of the paper would be helpful.

Response: We take the point of the reviewer that a somewhat more detailed introduction could be helpful.

We added the following text to the revised introduction:

'Field calibration of a spectrometer is not necessary for UV-visible absorption spectroscopy (see e.g. Platt and Stutz 2008), since the instrument can be calibrated by using high-resolution absorption cross section spectra of the particular gases. This is done by (1) determining the instrument function (IF) and (2) convolving a high resolution trace gas cross section spectrum with this IF and then (3) fitting the resulting trace gas cross section to measured spectra in order to obtain the trace gas CD. The details of this process are explained e.g. by Platt and Stutz (2008).

However, it may be tempting to perform the calibration process simply by recording the CD of an absorption cell filled with a known amount of trace gas brought into the light path of the instrument. This approach complicates the measurements and may introduce additional errors due to uncertainties in the trace gas CD in the cell.

Nevertheless this approach may work for a series of gases, like O₂, CO, CO₂, CH₄, which do not (at ambient temperature) undergo self-reaction and which are neither photolyzed by ambient solar radiation near the Earth's surface nor by the radiation typically used for their absorption spectroscopic measurement.

On the other hand, if a trace gas cell is used to determine absolute wavelength calibration of a spectrometer the absolute trace gas CD in the cell is usually not critical.'

- 44-45: Other cells and gases are mentioned; real-world examples should be provided. NO₂ is relatively unusual as a strongly absorbing gas in the actinic region of the solar terrestrial spectrum.

Response: See answers to the preceding comment of reviewer #2 on the introduction.

2. Optics

- Section 2.1 is unclear whether it refers to a cell containing absorbing gas or not. This should be explicit, and the Beer-Lambert dependence on pathlength for the single and multiple passes should be clearly described.

- 16: The authors explain in the figure caption, but not the text, where the figure of 2% enhanced SCD comes from. It is unclear how this relates to the absorption coefficient of the gas in the cell. In the case of strong absorption, the contribution of the multiple reflection becomes negligible even at relatively modest absorptions (e.g., $\exp(-aL) < 0.5$ means the first multiple pass of three times through the cell is $< 12\%$ of the original value. Values for other column densities would be instructive here.

Response: The reviewer is right here: The stated figure for the enhancement of the apparent CD in the cell due to multiple traverses are correct in the limit of a weak absorber. However, we also state in the text following Eq. (1) where the figure of 2% enhanced SCD (in the case of negligible trace gas absorption) comes from. In order to make the situation clear we changed the sentence following Eq. (1) to read:

'The reduction of the incoming intensity by $(1-R)^4$ or about 15% is probably of minor importance, however (if we neglect the absorption by the trace gas in the cell) a fraction of about $(1-R)^2 \cdot (R+R)^2 \approx 0.59\%$ of the incoming radiation and 0.69% of the transmitted radiation passes the cell three times (this effect will be lower at high trace gas optical densities and also could be reduced by adding anti-reflective coatings to the cell windows).'

3. Chemistry

- p.3, 43: A J value is provided for R1 but it is unclear where this comes from. The formula describing the photolysis rate and relationship to the actinic flux, quantum yield, and absorption spectrum should be provided. There is no recognition in the text that this key parameter, which drives all the subsequent chemistry, can be highly variable. It depends on whether this is direct sunlight, and how it depends on season, latitude, time of day, etc. It is also unclear how this J could relate to values for an active DOAS system with an artificial light source, or even whether such cells are used in this case. - The text does not describe whether the beam diameter completely or only partially fills the reference cell diameter. If the latter, then there is a more complex spatial dependence on the chemistry. Fortunately in this case, such a situation reduces the impact of the chemical reactions.

Response: We added text to better explain the role of photolysis and also included references (there are many in the literature) to field measurements of photolysis frequencies (Jones and Bayes, 1973 or Kraus and Hofzumahaus, 1998). Regarding the calculation of photolysis frequencies and their relationship to the integral over the product of the actinic flux, quantum yield, and absorption spectrum, we feel that this is common knowledge (see e.g. Platt and Stutz 2008) and not relevant here.

Although we discuss ways to minimize photolysis in the cell in section 5.2, we added text describing the variability of J1 (and the other photolysis frequencies as well). We also performed model calculations with the photolysis frequencies (i.e. J1, J17, J21) scaled to 1/10 (i.e. J1 = 0.0008/second) showing that the described effects (i.e. loss of NO₂) change surprisingly little with the actual value of the photolysis frequencies. We added the following text after R1:

'The above value for J1 is reached in full sunshine around noontime (see e.g. Jones and Bayes, 1973 or Kraus and Hofzumahaus, 1998), of course this figure (and in fact all photolysis frequencies in the cell, see Table 1, below) is highly variable, depending on solar zenith angle (i.e. latitude, season, and time of day), cloudiness and shading situation at the measurement site. In the case of active DOAS systems the photolysis frequencies will depend on the intensity of the light source and on the fraction of the cell cross-section area covered by the light beam. Nevertheless, it is frequently seen that calibration cells are used in full sunshine without any shielding, moreover, as it will be shown below (see section 4), the effects on the NO₂ chemistry are similar over a wide range of photolysis frequencies.'

- The text should clarify that the value for k_5 pertains to ambient pressures.

Response: We added the pressure specification (1.0E5 Pa).

- Example 2 has limited value because it excludes R5 (which has approximately the same rate as R4). In the limit, reformed NO₂ will eventually photolyse until NO is the sole product, but this process becomes increasingly slow. This is surely an important practical issue in the use of these cells.

Response: We do not quite agree here: As pointed out in our response to comment 8 of reviewer #1 it will depend on the circumstances whether R5 plays a role or not, but usually R5 will not be of importance.

- P6, 18: While the point made is correct, the time to attain equilibrium should be stated less precisely. The half-life is about 5 us.

Response: We think 'shorter than $1/k_8 \sim 7\text{us}$ ' is even more imprecise than 'about 5 us'.

- Fig. 3 may be simplified, but it seems odd to leave out these reactions: $\text{O} + \text{NO}$, $\text{O}_3 + \text{NO}_2$, and $2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3$

Response: Fig. 3 now shows two diagrams: a simple one (simple case) and a one showing the full chemistry.

- P.10, 35: State that this is a slow reaction in the gas phase

Response: We added the phrase 'in the gas phase' to the sentence.

- P11,21: "??" ??

Response: We inserted the correct value for k_{20} (as well as the pressure specification).

- $2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3$ is an important heterogeneous reaction and would certainly be expected to occur in reference cells, including under dry conditions as it is very difficult to get a completely dry well. This should be included in the simulations.

Response: We included the reaction as R23 in our simulations using the parameterisation proposed by Kleffmann et al., 1998. We assumed a typical cell (cylindrical, radius: 1cm, length: 5cm) as well as estimates of the amount of H₂O in this cell from assuming a monolayer of water at the inner surface of the cuvette.

We made the following changes to the text:

1) we changed R23 to $\text{NO}_2 + \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HONO}$

2) we added the following text after R23:

'Although this reaction appears to be second order in NO₂ several studies (e.g. by Kleffmann et al., 1998) found a first order dependence of HONO formation on the NO₂ concentration, probably because NO₂ reaction with NO₂ adsorbed at the wall is rate limiting. Therefore, heterogeneous reactions of N₂O₄ with water are probably not important.'

3) we changed the last sentence of the paragraph following R23 to read:

'Our model calculations actually show that all H₂O is ultimately (typically after a few hours in full sunshine) converted to HNO₃, sequestering equivalent amounts of NO₂ and water, thus no HONO will remain after this time.'

4) we added the following explanation of the parameterisation of R23 to the end of the first paragraph in section 4:

'The heterogeneous reaction (R23) was included in the simulation with the parameterisation proposed by Kleffmann et al., 1998 ($k = S/V * v * \gamma^{1/4}$, with uptake coefficient $\gamma = 1E-6$, the molecular velocity of NO₂ v and the surface to volume ratio S/V). We assumed a typical cell (cylindrical, radius: 1cm, length: 5cm, $S/V = 240 \text{ m}^{-1}$) as well as estimates of the amount of H₂O in this cell from assuming a monolayer of water at the inner surface of the cuvette. Of course - given the uncertainties in heterogeneous reactions - this approach can only provide a rough estimate of the HONO concentration in the cell.'

4. Simulations

- I find little value in Figs 4 & 5 which simulate simplified chemistry. What's the point? Simplifying cases of the full chemical system can be discussed in the text.

Response: We moved Figures 4 and 5 (now Figures 10 and 11) as well as the associated text to a new Appendix 2. The text at the beginning of section 4 'Gas Kinetic simulations' is modified accordingly.

- In contrast, Fig.6 could be split into several figures for presentation clarity.

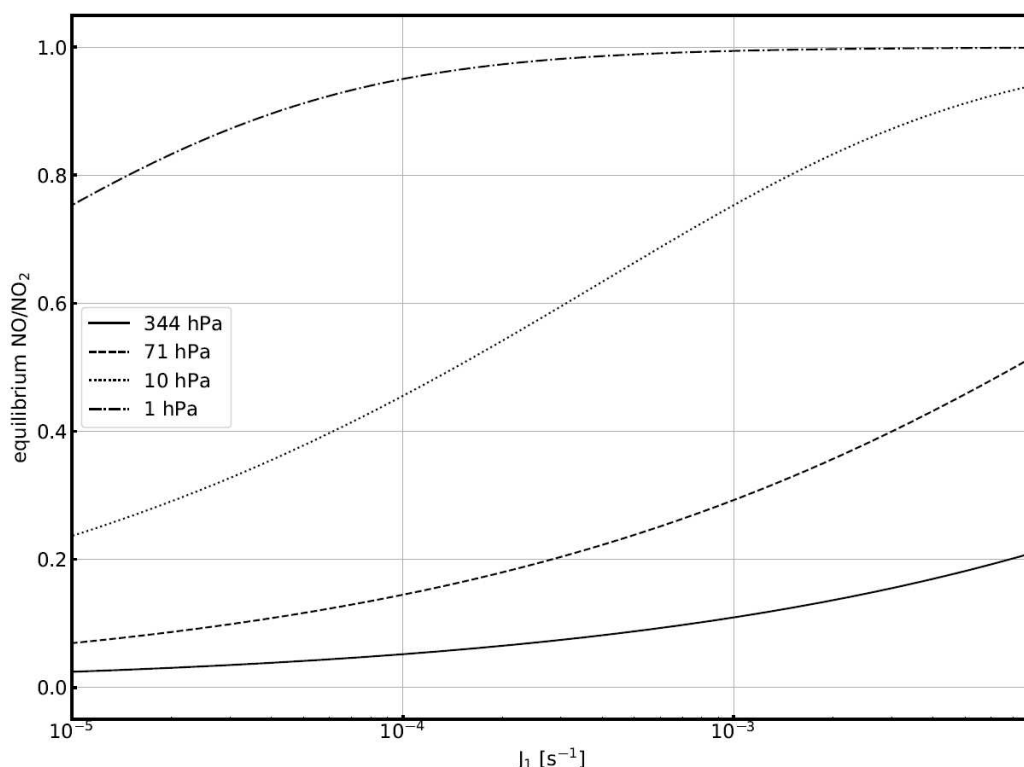
Response: We like this suggestion of the reviewer and split Fig. 6 into 5 individual figures (since Figures 4 and 5 are moved to Appendix 2 these new figures are now numbered 4 through 8.).

- The effect of changing J values was not investigated, though this would strongly influence the chemistry in the cells.

Response: We like to thank the reviewer for this comment, in fact in the discussion section we stress the importance of keeping photolysis frequencies to low levels. In order to make the situation more clear we studied the effect of different values for J by performing the calculations for the ambient level of J as well as for J/10. We added a trace for NO₂ with all photolysis frequencies scaled to 1/10 to figures (new numbering) 4 through 8. Note that all other trace gas levels shown are the results for calculations with the original value of J.

In fact, even very small values of J₁ can have a large effect on NO₂ levels in the cell as can be seen from the following figure showing equilibrium [NO]/[NO₂] from the analytical formula as a function of J₁ for four different initial NO₂ partial pressures.

For instance at 1 hPa initial NO₂ partial pressure (uppermost trace in the figure) at a J₁ of about 1/1000 of its value in full sunshine still >75% of the NO₂ is converted to NO:



Changes to the text of the manuscript: In the second to last paragraph of section 4 we added the following text:

'In order to study the effect of different photolysis frequencies we also performed model runs with all J-values scaled to 1/10 of the figures given in Table 1. The resulting temporal evolutions of NO₂ are also included in Figures 4 to 8 (note that the time series of all other species are for the J values as given in Table 1). As can be seen from these figures there is still a rather large loss of NO₂, even at J being only 1/10 of its value in full sunshine. This is due to the fact that the NO₂ loss scales only with the second or third root of the photolysis frequency (see analytical solutions in section 3 and appendix 1).'

5. Summary and conclusions

Another possibility is to use wedged windows for the cell (which would halve the reflections assuming internal window are parallel) or parallel windows angled sufficiently to avoid multiple passes.

Response: The case of angled windows is already mentioned in the summary section, however the suggestion to use wedged windows is a good idea. We added it near the end of section 5.

Minor comments:

Abstract:

21: "at" ! "using" / "for" etc. Awkward sentence.
25: particularly
p.3, 4: "oft" ! "of"
p3, 23: sentence fragment needs clarification

Response: We corrected all minor errors.