**Atmospheric
Measurement
Techniques
Discussions**

Interactive comment on "Linearisation of the effects of spectral shift and stretch in DOAS analysis" *by* S. Beirle et al.

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Reply to Reviewer 3

We thank the reviewer for the thorough and constructive comments. Below we repeat the original review in blue and reply to it point by point.

Reviewer Comment: This is an interesting paper, and addresses an issue of potential importance for remote sensing of trace gases using the new generation of hyperspectral instruments. I do not know if NO2 was the best choice of example, or if the relatively narrow wavelength window that was chosen is the

best. It is possible that, due to the spectral structure of this band of NO2, and given the sampling imposed, other windows would be more amenable to determination of the shift and stretch parameters. Relative to other trace gases, NO2's 420 nm band is quite strong, both in the large size of the spectral cross sections and the and its pronounced spectral line structure. Though NO2 is an important target of measurement, other important trace gas species are rather more difficult to retrieve, and, I should think, potentially more sensitive to wavelength calibration issues. Such species include formaldehyde, glyoxal, and BrO. Having showed the utility of the proposed method for doing the easier problem of NO2, the paper would certainly benefit from a treatment of one of these more difficult cases.

The size of the effect, within the suite of cases examined in this paper, for the example of NO2, are a few orders of magnitude smaller than current satellite instrument capabilities, both in detection limit and measurement uncertainty. This begs the question: In what cases would the implementation of the algorithms proposed and analyzed in this paper be important to improving the retrievals? The answer might lie in an analysis of more difficult cases than NO2, as I mentioned in the previous paragraph.

Authors' reply: We fully agree with the reviewer that our study has to be substantiated by an application of the linearisation scheme to more challenging trace gases. In the revised manuscript, we now also investigate the proposed linearisation for real satellite measurements for two routine retrievals at MPI-C Mainz, i.e. NO_2 and BrO.

The results for NO_2 are similar to those of the synthetic spectra. The results for BrO clearly demonstrate that the linearisation scheme works as well for minor trace gases, and substantiates the discussion of A_{Shift} versus B_{Shift} as well as the pre-shift in section 5, which were rather abstract in the AMTD paper. In the revised manuscript, the results of the NO_2/BrO fits for real satellite measurements are added in the new section 4.2, and the discussion is updated accordingly.

Reviewer Comment: I thought the discussion in Section 4.3 (Computation Time) was weak, as it suggested that the authors are a bit uncertain how the DOASIS software works. (E.g., "DOASIS seems to step into the Levenberg-Marquardt algorithm..." Certainly, this section is not a very extensive discussion

of the issue of computation time. For example, Levenberg-Marquardt is the only nonlinear least-squares algorithm considered. Others are commonly used. (I'm thinking, in particular, of the code developed by the group at the Harvard-Smithsonian Astrophysical Observatory, which, I believe, uses a Gauss- Newton method.) The authors note that the L-M algorithm has parameterized stopping conditions. For large-scale problems, some care must be given to parameter selection, based on the local "topography" in the vicinity of the minima. If the curvature is small, the minimum may be quite wide with respect to the fitting parameters being sought, so, whether solving linearly or nonlinearly, the solution is simply not well-determined. Though Section 4.3 is weak, I understand that to make it much less so would add quite a lot of discussion to the paper, and that might not be desirable. The discussion that is already in that section does make the point generally, but I would encourage the authors to try to improve it, if that can be done without adding a lot of words to the paper as it stands.

Authors' reply: We have tried to improve this section in the revised manuscript, but without substantial extension, to keep the focus on the key message that the linear fit is far faster than any non-linear solution, which is the most relevant justification for our linearization scheme from a practical point of view.
We modified the comparison of the linear fits from DOASIS vs. MATLAB as follows: "DOASIS does not directly provide the option of a linear fit; instead, the fitted parameters can be fixed (i.e. the shift can be set to 0). Though we can not comprehend the implementation details of DOASIS, we consider this to be the reason that DOASIS is slower for the "linear" fit compared to MATLAB."
A detailed discussion of the performance of LM and possible alternatives is beyond the scope of this study. LM is generally more robust than GN, which is only working for starting parameters close to the solution (see e.g. Platt and Stutz, 2008). GN is, on the other hand, slightly faster than LM, but not by orders of magnitude. In the revised manuscript, we mention the Gauss-Newton (GN) method as other important non-linear algorithm in the introduction.
We fully agree with the reviewer on potential ill-posed problems for low gradients. How-

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ever, this affects non-linear and linear algorithms likewise, and would be reflected by
the respective confidence intervals.

Reviewer Comment: p.8370, l.25: The description of the meaning of I_0 is vague: It is described as
the "initial" intensity of the light source, but I think it is better described as the irradiance falling on the
top of the atmosphere. Then, it is parenthetically referred to as the "reference spectrum", without further
comment (until much later in the paper) about what that means. This is an important point, and should not
be glossed over: The satellitebased instruments this reviewer is familiar with make _measurements_ of
the solar irradiance. In some cases, problems have been encountered when trying to use the measured
irradiances, and it has been necessary to use a fixed spectral irradiance, either based on a statistical
compilation of the instrument's own measurements, or on a reference spectrum based upon ground-
based measurements of solar irradiance.

Authors' reply: Though satellite measurements are the most likely target of our pro-
posed linearisation scheme, it is in general applicable for all kind of DOAS applications.
In the introduction, we focus on the aspect of the (non-)linearity of the DOAS equation,
and postpone the discussion of different DOAS applications to section 2.
For clarification, we modified the explanation of I_0 to:
"I_0 is the "reference spectrum", meaning either the intensity of an artificial light source
(active DOAS), the solar irradiance (satellite DOAS), or even a spectrum of scattered
sun light (MAX-DOAS)."
in the revised manuscript.

Reviewer Comment: p.8371, l.6: "Ring effect" and l.8: "Ring spectrum." This will probably be familiar
to those who have done DOAS-style retrievals, but not to everyone. The quotation marks are distracting,
and if one is going to use an assigned name, like this, then a reference (Chance & Spurr is the usual one)

should be included.

Authors' reply: A detailed explanation/discussion of the Ring effect is beyond the scope of this study. It is mentioned in the introduction as the most prominent example for a pseudo-absorber. We have added a reference to Solomon et al. and to Chance & Spurr for the "Ring spectrum" to the revised manuscript.

Reviewer Comment: p.8371, l.20: Three issues: (1) I'm not sure whether "instabilities of the light source" belongs on this list. In the wavelengths commonly used for backscatter ultravioletvisible measurement techniques, the sun is quite stable. To the extent that there are small variations, they could be extracted from the measured solar irradiances.

Authors' reply: This statement was not referring to the sun, but to artificial light sources like arc lamps. For clarification, we have added "for active DOAS" to this statement in the revised manuscript.

Reviewer Comment: (2) Reference cross sections (usually laboratory-measured) naturally have errors both in their wavelengths (directly relevant to the paper) and values (nsigma(nlambda)). Additionally, they are temperature-dependent, which means that they are different at different points along the light path, so Equation (1) is only an approximation.

Authors' reply: Uncertainties of the reference cross-sections would indeed directly affect any spectroscopic retrieval technique (including DOAS). A shifted cross-section, however, would affect the non-linear fit as well. As shown in Appendix A, a spectral misalignment of a cross-section can not be linearised analogously. However, "spectral shifts of σ probably do not have a high relevance in most DOAS applications, as cross-

sections can generally be measured in laboratory with high accuracy. Additionally, a shift could only significantly affect the DOAS analysis if the respective absorber has a high OD of several percent and narrow absorption lines. Thus, normally, spectral shifts of cross-sections can be neglected. But in the case of an analysis where spectral shifts of σ actually occur for a strong absorber, these shifts have either to be determined (and corrected) independently, or the DOAS analysis has to be performed by a non-linear algorithm." (Appendix A)

The temperature dependency of e.g. the NO_2 cross-section can be easily corrected a-posteriori as shown in Boersma et al., 2004.

Reviewer Comment: (3) The authors suggest that temperature changes of the spectrometer incur spectral misalignments, and that can certainly be true due to dimensional deformations of the components (especially, we imagine, those of a grating). Meanwhile, however, the calibration constants (dark current, gain) may also be temperature dependent, but in a different physical location, so that temperature may affect the radiometric calibration more than the wavelength calibration. The question is, Under what circumstances do the radiometric effects alias into wave- length offsets (shifts and/or squeezes) in the method proposed in this paper?

Authors' reply: (*) The reviewer lists some sophisticated effects potentially causing spectral structures which might interfere with the effects of a spectral shift. However, these effects would impact the DOAS approach in general, independent on the solution algorithm. Any effect causing physical or virtual wavelength offsets would be fitted as a shift, for the non-linear fit or the linear fit with pseudo-absorbers likewise. Thus, we do not discuss these effects in depth, as the focus of our study is to demonstrate that the spectral shift, commonly implemented as a non-linear parameter in DOAS analyses, can be linearised.

We have added the following statement to the beginning of section 2 of the revised manuscript:

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"Various effects could physically affect the pixel-wavelength allocation of the detector, like contraction/expansion due to temperature changes, or the Doppler effect for moving spectrometers. In addition, other effects (like interfering temperature effects on grating, dark current, and gain), might cause spectral structures similar to those of a spectral misalignment. In this study, we investigate how far the effects of spectral misalignments can be linearised. For this, the actual cause of the (physical or virtual) misalignment is not relevant."

Reviewer Comment: p.8372, l.4: In view of the small effect demonstrated (at least for NO2) in this paper, the first point is fairly easily overcome: An initial solution, using a linear fit algorithm (very fast), is refined in a subsequent nonlinear fitting step, starting from that solution. I suspect that this procedure would also avoid the problem of multiple solutions, though that is difficult to demonstrate rigorously. (This point is addressed by the authors, in passing, later in the paper)

Authors' reply: We fully agree with the reviewer that a linear fit should be used to find the initial values for a non-linear fit. This indeed turned out to speed-up our non-linear fit by 30% (see section 5.5). However, the statement on p.8372, l.4 is still true: the non-linear fit is still non-linear and requires the calculation of partial derivatives in each iteration. The better initial values just reduce the number of necessary iterations.

Reviewer Comment: p.8373, l.7: "insufficient mode mixing" – What does this mean?

Authors' reply: Light-sources applied in active DOAS measurements often feature a structured emission spectrum which is generally not isotropic. The non-isotropic light may cause systematic spectral structures in the measured optical density if not properly mixed (Stutz&Platt, 1997). These structures are partly compensated by the DOAS implementation by increasing the shift which can reach values of 0.02 nm.

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Reference: J. Stutz and U. Platt, Improving long-path differential optical absorption spectroscopy with a quartz-fiber mode mixer, Appl Opt. 36(6), 1105-1115, doi: 10.1364/AO.36.001105, 1997.

In the revised manuscript, however, we skipped this aspect, as it is rather special for active DOAS, which is not in the focus of our study, and obviously would need more comprehensive explanations as given in the AMTD manuscript.

Reviewer Comment: p.8374, l.22: For such a small (doppler) shift, would it not be just as effective to let it be determined by the proposed algorithm?

Authors' reply: The discussion of the Doppler effect and a pre-shifted set of references is substantiated in the revised paper by the additional application to actual satellite measurements for NO_2 and BrO. The proposed linearisation including A_{Shift} is indeed capable of correcting shifts of up to 0.02 nm with low SCD bias, both for NO_2 and BrO. But with a pre-shifted reference set, SCD biases are reduced further. This reduction e.g. allows us to use B_{Shift} instead of A_{Shift} for the BrO analysis. We clarify this in the discussion of the BrO fit results in the revised manuscript.

Reviewer Comment: p.8375, l.2: I think it would help the discussion, somewhat, to offer a comparison between the wavelength shift values and the typical line widths and line separations in the Fraunhofer structure.

Authors' reply: We added the following sentence to the beginning of section 2 in the revised manuscript:

"Typical misalignments are small (e.g. about 0.01 nm) compared to the measured spectral structures, which are determined by the detector resolution (e.g. about 0.55 nm FWHM for OMI). But, still, they can impair the DOAS retrieval of trace gases if being

ignored (see section 4)." "

Reviewer Comment: p.8383, l.9: The numbers stated–particularly, the NO2 bias, should be compared to the detection limits of the satellite (or other) instruments. For OMI, for example, for which both the data products (NASA's Standard Product and KNMI's DOMINO Product) are derived using a wider fitting window, the detection limit is on the order of 1-1.5E14 cm- 2. I expect that, with the narrower window, and different spectral sampling, the authors' choice of parameters, etc., the detection limit and typical measurement uncertainties would be somewhat larger, still. Thus, the improvement seen in the selected cases are at least a few orders of magnitude smaller.

Authors' reply: The reviewer is right in saying that the effects discussed in section 4.2 (now 4.1.2) and shown in Fig. 5 are far below the NO_2 detection limit, at least for small shifts. In the revised manuscript, we added an analysis of the dependency of the SCD bias on spectral shift for actual satellite retrievals (NO_2 and BrO). We follow the reviewer's suggestion and discuss these SCD biases with respect to the respective detection limits, which are also included in the new figures 7 and 8. However, we would like to point out that spatial/temporal means of satellite measurements can reveal significant gradients far below the detection limit. For instance, seasonal mean NO_2 maps reveal a ship-track in the Indian Ocean where enhancements of the order of 1e14 molec/cm2 can clearly be identified in the spatial patterns (Beirle et al., GRL, 2004). Thus, we argue that SCD biasses are only negligible if significantly lower (by e.g. one order of magnitude) than the detection limit. Otherwise, they could still affect satellite measurements if averaged over long time periods or large areas.

We start the discussion of the proposed linearisation scheme by analysing ideal spectra without any noise. Though unrealistic, this allows to verify the estimations of the order of magnitude of 1st and 2nd order effects (Eqs. 9 and 12). Thus, Fig. 5 is kept unchanged in the revised manuscript.

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Reviewer Comment: p.8385, l.21: It was stated in a previous section, that the maximum Doppler shift is ≈0.01 nm at 440 nm, and here it is stated that the linear fit works as well as the nonlinear one, even for such shifts, so this discussion (starting with "In cases") is confusing. It actually seems that the method described in this paper would automatically detect and correct for the Doppler shift, even if it is not predetermined, and the data "pre-shifted."

Authors' reply: We agree that the discussion of the Doppler shift and the application of a pre-shifted set of references was rather abstract in the AMTD paper, and the necessity of a pre-shift has not been clearly demonstrated. In the revised manuscript, the discussion of the Doppler shift is substantiated by the analysis of real satellite spectra. Indeed, a linear fit including A_{Shift} appropriately accounts for the Doppler shift, both for NO_2 and BrO. But a pre-shifted set of references would allow us to use B_{Shift} instead of A_{Shift}, even for BrO. Section 5 is updated accordingly.

Reviewer Comment: p.8387, l.20: I would not say the paper has made the case that the biases cannot be neglected. If they are well below the detection limit and the uncertainty of the retrieved SCDs, then they could certainly be neglected. Again, to make this case, I think one would have to look at trace gas retrievals that are more difficult than NO2.

Authors' reply: In the revised manuscript, the discussion is substantiated by the analysis of real measurements. However, the statement of p.8387, l.20 is already justified by the synthetic case study for NO_2: if shifts of 0.01 nm occur, but are not accounted for by a linear fit, the NO_2 SCD biases are about 2e15 molec/cm2 (Fig. 6), which is clearly above the detection limit!

Reviewer Comment: p.8390, l.4: Actually, there is a wavelength correction to be applied both in the case of the laboratory measurements and the remote sensing scheme, to account for the density-dependent

index of refraction of air. Furthermore, molecular absorbers' spectral structures are functions of temperature. I think it is possible that the difference between the expected and realized spectral structure could certainly alias as a spectral shift in the method described in this paper.

Authors' reply: See the reply above marked with (*).

Reviewer Comment: p.8390, l.18: This description is rather vague. There are any number of "spline interpolations," and I'm not sure what the following means: "we calculate the derivative as difference quotient for a small shift of 0.0001 pixel and apply spline interpolation for I."

Authors' reply: In the revised manuscript, the description of the derivative by spline interpolation now reads:
"... we calculate the derivative of the discrete functions I and I_0 by mimicking the difference quotient according to

$$y' = \frac{y(x+h) - y(x)}{h}, \tag{1}$$

where y is I or I_0, respectively, x is the (integer) pixel number, h is set to 0.0001 pixel, and $y(x+h)$ is derived by cubic spline interpolation of y."

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 8369, 2012.