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Atmospheric Measurement Techniques
Discussions

Interactive comment on "Quantification and parameterization of non-linearity effects by higher order sensitivity terms in scattered light Differential Optical Absorption Spectroscopy" *by* Jānis Puķīte and Thomas Wagner

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This is a very interesting paper addressing the field of differential optical absorption spectroscopy of the atmosphere. It is presumably of particular interest for the satellite limb measurement community. The underlying theory, developments and achieved improvements appear to be valid. The obtained improved results of limb satellite data have been validated using balloon measurements. The language is clear and structured. The manuscript fits well into the scope of the journal. I recommend publication after revision considering the points below.

General comments:

In general, the manuscript has very much content which makes reading quite difficult regarding the level of mathematical and technical detail. I highly recommend thinking about ways to shorten it, in particular thinking about which equations are necessary to increase readability, and to move some content into the appendix or supplement.

I highly encourage more qualitative physical explanations instead of deriving findings from pure math in order to clarify the meaning of equations and results and increase readability. Also sketches illustrating problems, light paths or viewing geometries would help.

Different problems of DOAS are mentioned in the introduction and theoretical sections, but not in a very structured way. It should be more clear what problems are present, which assumptions are normally made in standard DOAS, and what is addressed here (or already addressed in Pukite et al. 2010, see below), if possible in form of a table. For example, issues here are: a) light path is independent from absorption, i.e. the cross-section is no function of the light path (if it is, this is addressed in Sect. 4.3, for example) and can be separated from slant columns, b) Lambert-Beer is valid for transmission or a well-defined light path only whereas scattered light has an ensemble of more or less probable light paths contributing to the measurement, etc.

Some points of the current work are already addressed in Pukite et al. (2010) as well. This previous work is frequently mentioned but closer considered only in Sect. 5.1 on page 17. Before, it is not clear what the difference is and what the advantage of the suggestion in this work over Pukite et al. (2010) is. I highly encourage inserting a short section somewhere in the beginning of the manuscript summarizing the author's previous work (if relevant for or in the context of this work) and clearly state which new aspects are addressed here that were not addressed before (Sect 5.1 should be announced and referenced in this context).

The paper focuses strongly on limb geometry. How large is the improvement in other geometries (nadir, ground-based)? Are the suggested improvements negligible here?

I have some kind of "naive imagination" on this: For nadir observation it's clear that a slightly different light path will encounter more or less the same absorption. But for off-axis MAX-DOAS observations of tropospheric absorbers, photons on slightly different light paths can encounter substantial different absorptions. Does this mean MAX-DOAS measurements could benefit from the improvements suggested here as well?

How large is the effect of the instrument's field of view (FOV) typically? I guess it largely influences the ensemble of possible light paths (i.e. which paths can reach the detector) and therefore the effective light path? Could the authors shortly comment on the magnitude of this effect?

A comparison of the iterative two step approach with the linear two step approach and standard DOAS is performed. Other approaches are mentioned in the introduction and Sect. 5.2 (e.g. full retrieval approach). How does the method compare to these approaches (In the context of Fig. 18-19, Rozanov et al. (2011) is frequently mentioned)?

Although it sounds obvious, what is the reason that the second order term (Eq. 4) improves more than the third order etc.? Experimentally, this is shown in Fig. 3 I guess, but is it physically easy to see? Can it be that there are scenarios in which the third order term is negligible but the fourth order term is again important? In addition, the Taylor series approach should be shortly motivated (i.e. isn't it possible to directly use a non-linear fit on Eq.2 or are there other series approximating the function in Eq.2 leading to a more elegant equation than Eq.4)?

Specific and technical comments:

p.1, l.23-24: "…In this paper, we specifically define OD as the logarithm of Sun normalized radiance." Please better use something like "I_norm" to avoid confusion. In addition, later (Sect 3.5) the OD is again ln(I_0/I). This should be harmonized.

p.2, l.6 ff: "The non-lineartiy is strong … nadir observations of trace gases might be

substantially affected by non-linearity, especially if the tropospheric trace gas absorption is strong and the probability of multiple scattering is high". Does this mean, also MAX-DOAS measurements in polluted regions can be affected? (see also general comments above)

p.2, l.18: However,

p.3, l.12: "to take place" -> "to occur"

p.3, l. 13: "The intensity is basically the mean of this probability." This sounds a bit misleading. First, I guess intensity is not meant in terms of spectrum here, i.e. this is the intensity at a fixed wavelength? Second, probability is something between 0 and 1 without unit while intensity is a physical measure having a certain unit. This sentence should be rephrased or better rexplained.

p.3, l.17: "to take place" -> "to occur"

p.3, l.18-19: "The paths not originating from the Sun disk solid angle nor matching the instrument's aperture have zero weight". How is it possible that photons exist in the model that are not originating from the sun and where do they come from?

p.3, Eq. 2 and p.4, Eq. 4 (and in the surrounding text): In Eq. 2 it is beta_kj, in Eq. 4 beta_jk. Has this any meaning or is it just a mistake?

p.3, l.25: "box j" This is a three-dimensional simulation, i.e. j is not a layer but identifying a specific volume somewhere in the atmosphere, right?

Eq. 4 is obviously of key importance for the work presented here. I have no doubt that it is correct, but I started doing the Taylor expansion on a sheet of paper stopping very fast as it seemed to become lengthy. Was this performed by a program or by hand? If the latter, I would appreciate if the authors can provide just a scan-in of their Taylor expansion in the response (just for my own curiosity...).

p.4, Eq.4: Indices K, J etc. are not introduced as the Taylor expansion is not performed explicitly, (which is not necessary here of course) but one should mention what they are and where they come from.

p.4, l.11: tau_0 is the DOAS polynomial, right? This should be mentioned here (it comes only in the next section, but the question arises here). In addition, it should be mentioned that tau_0 is of smooth shape (and can therefore be described by a polynomial) as only scattering (lambdaˆ-4) is taken into account for the w_i (if this is true. . .).

p.4, l.13: "I_0 in this notation is not the solar irradiance." This is confusing for most readers as I guess they come from the DOAS field and are used to I_0 as being the reference spectrum. If I_0 is not important for the following, I would skip or at least rename it.

p.4, eq.5: Why the division by the sum of probabilities? Are they not normalized to 1 anyways?

p.5, l.22 "due to the reason of readability" better: "for better readability"

p.6, l. 3 please insert an "and" between "order" and "a_p"

p.6, l.5: wavelength-dependent (here and everywhere else)

p.6, l.12-14: ". . . become less probable". Does this mean L_j in Eq. 13 becomes smaller and therefore also the slant column? (This needs more explanation; the question is what is not considered in the linear model leading to too small slant columns).

p.6, l. 20: Which two problems (this is not clear from the paragraph before).

p.7, l.4-5 and eq. 14: ". . . also the wavelength dependence . . . can be approximated by polynomial functions". If neglecting tau_2 and tau_3 and deleting the sum over lambdaˆp in tau_1, the DOAS equation is left in the usual form; the authors should explain where the polynomial in tau_1 is coming from (most likely the w_i in Eq. 5 I guess?). Is this the wavelength-dependence of the SC already addressed in Pukite et

al. (2010)? If yes, please mention. Second question: This approximation by polynomial functions is only possible because the effective light paths take into account only pure scattering (no absorptions), i.e. predominantly Rayleigh scattering with lambdaˆ-4 dependence?

p.7, l. 8: "as well as" (second "as" is missing)

p.7, l.8: ". . . are fit parameters". Normally, fit parameters are slant columns and coefficients (i.e. quantities that are obtained from the fit) while cross sections (as well as products of the cross sections etc.) are input to the fit.

Sect. 3.2: There are a lot of slant columns here. Which one is the slant column of interest (e.g. sum of all?)

p. 8, l. 11: "altogether" can be deleted

Sect. 3.3 and Eq. 18: Does this mean that from sum over k (absorbers) in Eq. 4 not all terms are needed in the end but only strong absorbers whose absorption structures coincide with another absorber? If yes, please mention.

p.8, l.18-19: Pukite et al. (2010) is referred to but not motivated or introduced before (see general comments above).

p.9, l.4-6 and Fig. 1: ". . . see Table 4.1 in Pukite (2010)". Same problem as above. In addition, a calculation for a specific scenario is mentioned here but not described (the reader has to read Pukite et al. 2010 for details). This is not sufficient.

Sect. 3.3.3 The second paragraph only explains what the second order effective light path physically mean. This information should be moved to the beginning.

p.9, l.24-25: ". . . contribution of the light path is zero". For better understanding: One has then a tensor of the second order effective light paths and only adjacent boxes close to the most probable light paths have values considerably larger than zero?

p.10, l.10: In practice,

p.10, l.15: For illustration,

p.10, l.15 ff. Again, no word is spent about what is shown (measurement geometry).

Sect. 3.4 Maybe this is a candidate to be moved into appendix or supplement getting rid of 3 equations? The authors could replace this section by a qualitative description.

p.11, l.16: "The fundamental assumption by the standard DOAS …": I wouldn't call this an assumption, but the fit window is selected in a way that the absorber of interest has unique spectral features. And I guess that this applies not only to standard DOAS, but also for the more sophisticated approach presented in this manuscript?

p.11, l.17 and Eq. 28: In contrast to the beginning of the manuscript, the intensity here is not sun-normalized, i.e. the OD is no longer –ln(I), but ln(I_0/I). I suggest to harmonize this by not using sun-normalized intensities in the beginning.

p.11, l.20 "In order to improve the fit results sometimes differential cross-sections are applied…" Using differential or non-differential cross-sections (in classical DOAS) should make no difference as the DOAS equation is a sum, i.e. if subtracting a polynomial from cross-sections before the fit should only result in a different fitted DOAS polynomial.

p.11, l.21-22: "has its own fingerprint not mixed with another absorber". I think cross-sections of different absorbers are never 100% orthogonal to each other in a DOAS fit which still works as the problem is largely overdetermined? If the cross-sections are too identical, shouldn't this result in a large error or completely failed matrix inversion?

p.11, l.23-25: This is true, very interesting and of key importance. However, this attribution of fingerprints to the product of absorbers follows only from Taylor series expansion and mathematical equations. I would again encourage a physical explanation here.

p.11. l.26 – p.12 l.1: This paragraph should be rephrased to increase readability.

p.12, Eq.29: What does the c (suffix of tau) mean?

p.12, l.18: and Fig. 3: "disagreement (rest OD)" is better called simply "difference" (also in caption of Fig.3). In Fig. 3, why are there so few red dots whereas the inter-correlative terms are much smoother?

p.15, l.1: Therefore,

p.15, l.9: "or at a given background scenario". This is then a bit in disagreement to Eq. 4 where the Taylor expansion was performed around beta = 0 and somewhere in the beginning it was said that the simulation of photon paths were made without absorption.

p.15, l.18: For example, one can…

Fig. 4: This is an interesting figure. The relation appears to be quite linear. Would this be expected taken into account the wavelength dependencies of Rayleigh and Mie scattering?

p.15, l.23: "By performing the Taylor series expansion with respect to absorption…" This means, the Taylor series expansion was performed not around beta = 0?

p.16, l.1: Here,

p.16, l.9: The comma between "Fig.5" and "a" is confusing…

p.16, l.10: Why 545.22 nm (why not simply 545 nm)?

Fig. 5 c and d: Why these uneven wavelengths (and are the numerous decimals really needed here)?

Sect. 5.1: Only here (page 17) the previous Pukite et al. (2010) is considered more closely (see general comments above).

p.17, l7: However,

p.17, l.23: "…Term 4 can be neglected for weak absorbers". It can be neglected because sigma_Y is so small or c_Y?

p.18, l.3: inter-correlative

p.18, l.6: Is this fit window a common recommendation for any trace gas or just selected for demonstration purposes because of the O3 absorption (because the effect on NO2 is discussed here)? I.e. a reference would be beneficial.

p.18, l.19: For the statistical analysis,

Sect. 5.2: A reference to a full retrieval approach (or some existing work) would be beneficial (some references were already given in the introduction but missing here).

p.19, l.17: Better rephrasing the sentence to e.g. "Similar to the previous method, AMF calculations for every spectral point are required, . . ." Why doesn't a parameterization as suggested before work here?

p.19, l.23: wavelength (not wavelengths)

p.20, Eq.47: To avoid confusion, please mention what suffixes g, f, and I are.

p.20, l.14: ". . . where sigma_gX are the fitted parameters. . ." Again, I think the fitted parameters are not cross-sections (input to the fit) but the fitted quantities, i.e. slant columns etc.

p.20, l.23: better ". . . to allow the use . . ."

p.20, Eq.48: The suffix "a" indicates here the apriori (if yes, please mention, otherwise please clarify)?

p.21, l.8 please harmonize writing of "broadband" or "broad band" etc.

p.21, l.20 and Figs. 10 and 11: Which scenario is this? (Please mention even if it is still the same).

p.21, l.24-25: Better "Some remaining absorption can still be seen for ozone . . ."

p.21, l.26-27: "Also an almost complete removal of systematic residual structures is observed for the UV fit window; the rest is most likely attributed to higher order effects

or simulation errors." In Fig. 10 the residual structure shows a distinct feature around 338 nm. Could higher order effects explain such a feature which is restricted to only a few wavelengths at the edge of the fit window? This structure is already present for the initial retrieval and not removed while the other structures are largely removed. In contrast, the Vis example (Fig. 11) shows a residual looking like noise. In addition, the Vis residual is much larger than the UV residual. Could the authors comment on this?

p.22, l.4: For this retrieval, . . . (and remove the comma after "shown")

p.24, l.17 and Fig. 14: ". . . larger discrepancies with respect to the true profiles are obtained." Is there an explanation for this? As one more BrO and two more ozone bands are included, one would assume naively that the result improves.

p.25, l.2: from different approaches

p.27, l.9: "linear algorithm (gray line)" According to the figure's legend it is the green line.

p.28, l.3: Please harmonize use of "temperature dependence" and "temperature dependency"

p.29 ff: The whole 1.5 pages of the conclusion section consists of a single paragraph making reading difficult. More structure would be beneficial.

Tab. 2: (Similar question as above): Do the fit settings follow some recommendation (reference)? Especially the polynomial order seems to be quite low for a UV fit.

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