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Atmospheric Measurement Techniques Discussions

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

Anonymous Referee #3

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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.

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.

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

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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 satellite-based 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.

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.

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 ultraviolet-visible measurement techniques, the sun is quite stable. To the extent that there are small variations, they could be extracted from the measured solar irradiances.

(2) Reference cross sections (usually laboratory-measured) naturally have errors both in their wavelengths (directly relevant to the paper) and values (\sigma(\lambda)). 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.

(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-

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length offsets (shifts and/or squeezes) in the method proposed in this paper?

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)

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

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?

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.

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 cmˆ-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.

p.8385, l.21: It was stated in a previous section, that the maximum Doppler shift is $\sim$ 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."

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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.

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.

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."

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