

Interactive comment on “The impact of vibrational Raman scattering of air on DOAS measurements of atmospheric trace gases” by J. Lampel et al.

Anonymous Referee #2

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The manuscript entitled “The impact of vibrational Raman scattering of air on DOAS measurements of atmospheric trace gases” by J. Lampel et al. describes the effect of vibrational Raman scattering (VRS) of N₂ and O₂ on ground based MAX-DOAS measurements. In this work, a method is developed to correct for VRS and may be important to consider it in UV-Vis passive remote sensing measurements. I recommend publication after addressing the main points below:

Major comments:

The manuscript presents a quantitative description of the VRS and the authors suggest its contribution it is important in passive DOAS application (satellite, airborne, and ground-based MAXDOAS). The authors suggest that the correction of VRS needs to

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be addressed in the retrieval of NO₂, IO, glyoxal (CHOCHO), and water vapor (H₂O). However, the present manuscript/results partially supports this. The only measurements used to test the effect of the VRS is the data recorded during the research cruise M91 during SOPRAN. The cruise was carried out along transects from the open ocean to the coast of Peru using a single spectrometer. The major comments are as follow:

1) Many times the authors suggest that the VRS should be included in the retrieval of CHOCHO, and IO. However, based on the few results shown here the contribution of VRS does not change significantly the dSCDs of IO, and CHOCHO. The latest, which is always below detection limit. It is mentioned that the RMS decreased in both cases, as expected since an additional cross section is fitted. If the authors suggest that VRS contributes significantly for both gases I would recommend to show the effect of VRS in the retrievals of CHOCHO and IO under different environments (to also avoid water VRS).

2) It looks like the effect of VRS may be important just when the residuals achieved during the DOAS fit are photon-shot noise limited. The manuscript does not show how possible instrumental issues (such as instabilities, stray light) are discarded with the single spectrometer used in this work. In order to make transparent the effect of the VRS I recommend to carry on an explicit description of possible instrumental issues that may correlate with the VRS. If possible, maybe showing results under different environments (see major comment #1) with different spectrometers. Showing results under different environments/instruments will enhanced the quality of the manuscript, in addition will show consistency of the quantitative effect of VRS in the retrieval of weak absorbers.

3) The current DOAS analysis considers quite a lot of manipulation, for example, two rings are fitted all cross sections are shifted and squeezed. In principle, one might expect more details of why all of this is needed and how it may correlate with the VRS, however it is barely mentioned. Since this is an initial attempt to know the effect of

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N₂/O₂ VRS I suggest to clearly perform a thorough analysis of cross-talk of the VRS with several DOAS settings.

4) In order to identify clearly the VRS the authors use 16- co-added spectra achieving low RMS and 2h time resolution. However, for real MAX-DOAS measurement this noise level would not be reached, would not be ideal and/or recommended, besides the expected changes in the atmospheric conditions. I recommend to expand/describe the effect of N₂/O₂ VRS under real conditions where sometimes photon shot noise limiting regime is not achieved. Again, showing quantitative results of the effect of N₂/O₂ VRS in different environments and regular operation will improve the quality of the manuscript.

5) In the current form, the manuscript is very hard to read (see also minor details below). I think this is partially due to several reasons: (1) organization of the manuscript, for example, you start describing DOAS setting without describing the aim of the analysis, species, and window range; (2) important information is missing (e.g. how the instrument is characterized to make sure is photon shot noise limited, acronyms are missing).

6) In the current manuscript the impact of the VRS is described in terms of an average RMS and OD (dSCD) effect. Honestly, I was expecting results in terms of some type of time series along the cruise. I wonder if you see a geometry effect (e.g., viewing angle, elevation angle, etc) and how aerosol may affect the VRS magnitude. Also, probably discussion of how current radiative transfer model handle the VRS would be interesting to see.

Specific observations:

Abstract: The abstract introduces the motivation of this work and explain shortly (nicely) the importance of the vibrational Raman scattering in the DOAS analysis. However contains little information about how the impact of the vibrational Raman is evaluated. In general, the abstract does not follow consistency, I suggest to re-structure the ab-

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stract following a concise description of the work performed here including a better description of the approach, which is missing, main results (from the research cruise) for trace gases, and implications. This might be important because it introduces potential readers to read the full manuscript.

Page 3, line 3: I suggest to list the important trace gases that may be affected by the VRS. If preferably all the trace gases measured by passive DOAS can be listed. I do not see a reason to list here, for example, OCIO, and BrO, and not IO, CHOCHO that are the gases you are presenting results.

Page 3, line 9: Formulas are used for all trace gases listed before, however glyoxal, and water vapour are written with names. I suggest to use "name (formula)" for trace gases you think is necessary, then adopt formulas along the manuscript.

Page 3, line 20: the correct way to use "i.e" is "i.e.". Correct accordingly in the manuscript.

Page 4, line 9: Figure 1 introduces the VRS, hence it is important to describe the calculations or method used to obtain the cross sections shown in Fig 1. This is not mentioned at all.

Page 4, line 22: it is mentioned that water vapor is around 5-10 times as strong as the VRS, however according with the cross sections of Fig 1, and the cross section magnitude given in the text it should be 50-100 times higher. Please clarify.

Page 5, lines 5-15: The quantitative description in section 2 is quite choppy and difficult to follow. In my opinion the quantitative description should start with equation 5, before even introducing the partitioning functions.

Page 10, line 11: There is not such Mie and Rayleigh extinction. In my opinion, this is a common misconception carried out on the field. Mie theory, for example, is an analytical solution of Maxwell's equations for scattering of spherical particles. In short, the extinction is not caused by Mie. I would not call Mie and Rayleigh extinction, instead

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use extinction from particles and molecules.

Page 12, line 13: Is there a technical reason of using 40deg as the elevation angle for the reference. Normally, the zenith spectra is used to remove stratospheric absorbers. Please elaborate why this elevation angle is used and how this may affect the results.

Page 12, equation 18. I would remove equation 18. It is already introduced in equation 16.

Page 12, section 3.2 (lines 16-20): It is mentioned that 16 elevation angles were added to reduce noise. However it is not mentioned at all the window range aiming here, what species are you interested?. Also, considering the cruise track from figure 4 I would expect quite considerable different atmospheric conditions within the two hours. Is there any evidence of stability in the two hours time resolution achieved by adding 16 elevation angles?. Additionally, do you expect a change in the Ring effect within this two hours?.

Page 13, line 13: Please elaborate more on the use of the second Ring used here. The reference is given, however, it is important to expand details since possible cross correlation may exist with the VRS. Was this orthogonalized?

Page 13, lines 5-6: It is not clear whether the single mercury emission line at 404.656 was used along all wavelength. In other words, do you assume that the instrumental line shape is constant along different wavelengths?.

Page 13, lines 7-12: Describe what wavelength you are interested first, then explain why O3 is not necessary. On the same paragraph it is mentioned: "The zeroth order intensity offset correction was realized by including an inverse reference spectrum in the DOAS fit". Please expand how the inverse of the reference corrects for the offset. Do you find a cross talk between the offset and N2/O2 VRS?.

Page 13, lines 24-27: The detection limit of glyoxal is estimated based on RMS, however up to know the window range is not mentioned. I suggest introduce the fitting

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window before, for both the UV and Vis and list the species you are interested.

Page 14, lines 4-6: The fitting window is mentioned here, however I realize that the strong glyoxal band is not covered here, please clarify if this window is used to estimate the detection limit from the previous paragraph. According with this paragraph you suggest that glyoxal dSCDs are way below past studies, however it is not clear if you are aiming to retrieve glyoxal, please clarify if you aim to retrieve glyoxal?, if so, please explain why this window range was used. Do you see higher glyoxal if using the stronger band?

Page 12, lines: 7-12. It is mentioned that shift and squeeze are used for all the cross sections (except Ring). Then at the end of the paragraph it is mentioned that no significant differences were found when using both the shift and squeeze. I would expect some kind of sensitivity of the shift and squeeze here, especially because the VRS are shifted structures and for the low optical densities. I really would recommend a thorough sensitivity study of these settings.

Page 15, lines: 1-2: If I understand this sentence (and last paragraph) the vibrational-rotational transitions (JVRS) is calculated with the software DOASIS, is this correct?. If so, is there a reference where this has been done previously?.

Page 15, equation 20: It is not clear why exactly you introduce $I_0 = I \cdot x \cdot H$ if I_0 is not really introduced in equation 20. Somehow this paragraph does not read properly.

Page 15, lines 12-15: I would change in the manuscript "measurement data" to just "measurements".

Page 17, lines 5-15: Expand the effect of the intensity offset correction applied, how was this determined?. The next sentence does not read properly, "the size of the intensity offset correction, exposure time and number of scans to test if dark current/offset correction spectra might contribute to the residual."

Page 17, lines 24-25: The sentence: "In other vectors corresponding to other absorbers

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or parameters the structure associated with N₂=O₂-VRS was not found.” Is not clear. Do you mean that the VRS was important for some spectra and not for other?.

Page 18, lines: 19-20: Do you mean theoretical calculations?. In general I recommend to expand this description. It is important to understand the dependence on solar geometry. With the current description is not clear whether the VRS is more important for angles close to the sun. Also, in the same paragraph (and table 6) it is not described how $d\sigma(\Theta)/d\Omega$ was calculated. Do you have to use Mie theory?

Page 20, line 8: “leads” is mentioned twice.

Page 20, lines 7-9: According with the sentence here the analysis of NO₂ in the wavelength range of 432-460 nm leads to an underestimation of NO₂, however I do not see how this was concluded, please expand this description. Also, when comparing the NO₂ dSCDs the wavelength dependence should be considered, is this considered here?. I suggest to present quantitatively comparison of the NO₂ dSCD using the IO wavelength intervals (considering the VRS) and the usual fit window (Peters et al., 2012) where the VRS may not be as important (and considering the dSCD wavelength dependence).

Figures:

Figure 5: The value of the intensity offset is 3.3×10^4 , could you please describe how to interpret this big number?

Figure 9: how is the x-axis calculated?. I understand it as the NO₂ dSCDs derived from one of the analysis but it is not clear which one. If I understand properly, the “including VRS”, and “Reference fit” are two different ways to correct for VRS, is this correct?. Black lines are not described.

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