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Comment

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 #1

Received and published: 27 April 2015

This is a very interesting paper concerning the inelastic vibrational Raman scattering effect (VRS) in ground-based DOAS measurements of sunlight scattered in the atmosphere. While this effect was theoretically known, its presence was so far only demonstrated in measurements in or over liquid water (as VRS in liquid water is much stronger) but thought to be negligible for pure atmospheric scattering. Thus, the findings of this paper are of high interest and potential use for future DOAS analysis of small absorbers and are therefore well suited for publication. However, I have some major questions/concerns/comments that need to be answered / addressed before final publication.

General comments:

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1) I suggest to point out more clearly (already in the abstract) that VRS was so far experimentally studied only for liquid water (where it is stronger) while for the atmosphere it was in theory known to be present as well but always neglected for DOAS and no experimental evidence (in DOAS) was found so far (as this is the novel aspect of the present paper).

2) A major problem of this paper is that the retrieval of VRS as well as proof of its presence was performed using measurements from a ship campaign, i.e. from measurements over water having a potential contamination of spectral structures introduced by liquid water VRS. It is not clear to me, why the author's didn't use measurements over land which are for sure free of possible liquid water VRS. However, for final publication it is absolutely necessary to include examples demonstrating the presence of N₂ and O₂ VRS in measurements over land in order to destroy these concerns (the authors briefly mention that they included but didn't successfully find a simulated liquid water VRS spectrum from Grossmann et al. 2013 which is not further discussed and in my eyes not sufficient).

3) A consequence of the large shift of VRS (several tens of nm) is that in addition to filling in and Fraunhofer ghosts also shifts of larger structures of the spectrum occur. For example, in a recent study of Peters et al. 2014, a clear step in optical densities around 460 nm was found arising from the increase of the sunlight spectrum shortly before 400 nm which was shifted by approx. 60 nm due to VRS in liquid water. For N₂, the shift is approx. 30-40 nm, i.e. a similar step should be observable at 430-440 nm in the optical densities shown here. However, it is not very clear to see. Is this only because these are differential structures and the broad band N₂ VRS structures are removed from the polynomial in the rather small fit window (e.g. 20 nm in Fig. 5)? (By the way, do I see optical densities or differential optical densities here?). In addition, I see this step for liq. water in Fig. 3 (right edge of the lowermost subplot), but not for N₂ and O₂. Is there any effect that prevents this structure to be shifted to approx. 430 nm for N₂?

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4) To the previous point(s): In a larger fit window (extending 460 nm for the upper edge), is there a step around 460 nm in the measurements from ship? Because if there is, this would indicate contribution of liquid water VRS to the measurements, and vice versa the non-existence of this structure would be a good way to proof the correctness of the performed work. Furthermore, in this case it is interesting that liq. water VRS is obviously not present over non-clean (coastal) water surfaces. I think this is worth to be mentioned.

5a) Effects in trace gas retrievals: I understand that for small absorbers like IO any effect larger or equal the size of the trace gas signal has to be included in the fit. However, I have concerns when I see a fit containing two (RRS) Ring spectra, 2 VRS spectra and straylight correction which all look similar as compensating mainly for residual Fraunhofer structures (incompletely removed by I/IO). Is there really enough information that all these effects can be distinguished? 5b) This isn't a larger problem if no interest in the physical interpretation of SC_Ring, SC_N2VRS, etc. exists and the only aim is to remove the sum of all these "disturbing" effects. Anyways, misfits of IO can be introduced if there is a linear dependence between the IO cross section and (linear combinations of) Ring and VRS spectra. Did the authors check for this? 5c) Maybe related: I heard DOAS people often state the matrix inversion will fail (or produce very large fit errors) if the cross sections included are too similar and do not spend too much time thinking about how reasonable the outcome of the DOAS fit is. However, the inverse of a matrix only exists if all rows (cross sections) are orthogonal which is likely never the case for a DOAS fit. I think people therefore calculate the pseudo inverse but doesn't this bring back the original problem? Is there any indication reflecting the reliability of retrieved trace gas slant columns?

6) There is a recent study about VRS from liquid water in MAX-DOAS measurements over clean ocean surfaces (Peters et al., 2014, AMT). This paper is cited, but in a wrong context. This is a pity since many points complement each other nicely and both papers in combination provide an overall view about the compensation of VRS effects

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in DOAS measurements. In particular:

a) Fig. 3 and P. 3427, I. 22: The finding that the small-band structures of liq. water VRS OD are very similar to the intensity offset normally applied in DOAS fits match nicely to a major finding in Peters et al. 2014 and implies that they are probably compensated automatically in a DOAS analysis. Fig. 3 also indicates that there is a broad-band liq. water VRS structure which was also found in Peters et al 2014 where it was successfully compensated (not achievable by the DOAS polynomial). Both can be mentioned I think.

b) In contrast, N₂ and O₂ VRS are not so similar to the intensity offset (but smaller than liq. water VRS) so that their small-band structures are not compensated automatically by the intensity offset (I guess especially due to Fraunhofer ghosts?).

c) The influence of VRS on NO₂ slant columns is also in agreement with the mentioned paper but the difference is one order of magnitude smaller (most likely because N₂ VRS is smaller than liq. water VRS) which can be mentioned.

d) As here N₂ VRS was successfully retrieved over water (close to the coast) and liq. water VRS was successfully not found there (see points above), a major finding is that liq. water VRS is obviously not present in measurements over non-clear water surfaces and thus needs not to be compensated there in contrast to measurements over the clean tropical ocean where it is stronger than N₂ VRS and needs to be compensated even if non-co-added measurements are analyzed (as in Peters et al, 2014). This should be mentioned. In summary recommendations (maybe in form of a table) could be given about what VRS effects limit the DOAS retrieval in which environment in order to give recommendations for future DOAS measurements.

7) I am still a bit confused by Sect. 3.2. Although I see improvements compared to the original version, there is still a mix of intensities I, I₀, J which are sometimes measured spectra, sometimes a solar atlas, sometimes calculated spectra based on either measured spectra or solar atlas (and I guess “Fraunhofer reference spectrum”

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means the measured reference spectrum I0, or is it any extraterrestrial spectrum, i.e. a solar atlas?). I still encourage making a table clarifying what is what (especially measurement or from literature). Furthermore (P. 3436, L. 12 ff), I don't understand why the calculation of intensity correction spectra due to VRS can be based on measured spectra as these already contain the effect of inelastic scattering. In addition, any measured spectrum contains absorption structures (which can be filled-in) and I think in reality it depends on where the inelastic scattering happens, which is most likely after stratospheric absorptions (and maybe parts of tropospheric absorptions) but before the majority of tropospheric absorptions happen. So in principle I would assume that a radiative transfer model is required?

8) Sect. 5: Although I have no doubt that findings and recommendations are true, it is important that these findings apply to 2-hour averages (i.e. measurements in that random noise is averaged away) and the resulting optical density is in the order of only $2.5E-4$. I think it is honest to clearly indicate this (admitting that this reduces a bit the potential use) because otherwise people possibly start to introduce the VRS cross-sections in single measurements of several seconds integration time where it is practically not detectable but might introduce interferences with other cross-sections. Maybe it is possible to state this at the end of Sect. 5. In addition: Throughout the manuscript VRRS is discussed but in Figs. 5 and 8 not shown and at some point mentioned to be compensated by the intensity offset (and VRRS points in Fig. 1 are two orders of magnitude smaller than VRS points). Does this mean VRRS was not detected even in 2h averages? If yes, the conclusion is that one has not to be concerned about VRRS for current instruments? Please clearly state so in the revised manuscript, if this is true.

9) It would be a benefit if the authors could provide a table with their N2 VRS spectrum (in 0.1 nm resolution it shouldn't be a too big table; maybe it can be provided also in the supplement).

Specific comments:

P. 3424, Abstract: For which wavelength range do the numbers provided here apply?

P. 3424, l. 6: "...and absorptions of atmospheric constituents" please add: "... if the inelastic scattering happens after the absorption".

P. 3424, l. 11 ... "filling in of Fraunhofer lines, additional to RRS"... please add: "...as well as shifts of broad-band structures (since the shift is very large compared to RRS)".

P. 3425., l.6 ff: What about direct-sun measurements?

P. 3425, l. 7: "The MAX-DOAS principle allows to reach higher sensitivity... " This doesn't somehow fit to the sentence before where you already mentioned off-axis measurements. Maybe this could be rephrased.

P. 3425, l.14: "... in particular narrow lines..." doesn't this depend on the width of RRS shift in relation to the Fraunhofer line width (expecting a largest effect if the shift is about half the Fraunhofer line width)?

P. 3425, l. 15: I think there were some Russians discovered the Ring effect even before Ring and Grainger who could be credited here.

P. 3425, l. 20: Here you are using "filling in", on p. 3425, l. 5 "filling-in". Please use only one form.

P. 3426, l.21: Isn't there also a mode around 1600 cm⁻¹ for water vapour (see above)?

P. 3427, l.16-25 and Fig. 2: I was first confused and realized only slowly that here the authors discuss the different spectra after suffering N₂, O₂, H₂O, liquid water inelastic scattering and NOT optical densities. This should be stated more clear as in the paragraphs before optical densities and filling-in effects are discussed which appear not in Fig.2 but only in the next step then in Fig. 3 (hope, I got it right now)? Same paragraph: Does this mean due to the smearing liq. water VRS produces no Fraunhofer ghosts? If yes, please mention because it is an important difference.

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P. 3427, l. 28: In Fig. 1 the individual peaks (of RRS around VRS) seem to be relatively close to each other. If the Fraunhofer line width is broader than the difference between two RRS lines (around a certain VRS line) wouldn't the resulting Fraunhofer ghost line produced by N2 VRRS be somewhat smeared as well?

P. 3427, l. 6-8: "... compensates for a large fraction ... in the atmosphere". Please mention that it compensates liq. water VRS even more (see also general comments above).

P. 3428, Eq. 1: How is the light path estimated (because later on P. 3436 this formula is used to calculate the additional intensity spectra due to VRS)?

P. 3429, l. 1-2: Please mention that "differential" denotes here the real mathematical meaning and not the high frequency part of something (what the DOAS community is used to).

P. 3432, l. 10: I thought $\ln(I_0/I)$ is usually referred to as "Optical depth" (sum of all effects) while "Optical density" refers to a specific effect/trace gas?

P. 3421, l. 14: Please mention that the broad-band part is accounted for by a polynomial fitted (together with trace gas cross sections) to the measured OD.

P. 3432 equation 17: Eq. 17 is only true if the concentration does not vary along the light path, which is not true for atmospheric absorbers and leads to the concept of slant columns (which need to be introduced anyways).

P. 3433, l.21: Until which elevation angle was the active correction performed?

P.3434, l. 9: Please mention also the name "slit function" used by many people.

P. 3435, l. 10: How often were these measurements performed? Were there any changes of the instrument function or wavelength calibration observed?

P. 3434, l. 13: Why 40° elevation and not a zenith spectrum as reference I0? The absorption signal of tropospheric absorbers in measured OD will be larger then.

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P. 3434, l. 16 ff: In which time resolution results co-adding 16 scanning sequences and what would be the influence of a change in SZA and relative azimuth during this period? From the cruise track plot it is clear that the ship's course changed from time to time. If such a change occurs within the average of 16 sequences the viewing azimuth changes dramatically.

P. 3435, l. 1 ff: So the first Ring spectrum is a normalized (according to Wagner et al. 2009) accounting for inelastic (RRS) single scattering probability while the second one accounts for multiple scattering? Was there any orthogonalisation applied?

P. 3435, l. 17-18: Peters et al. 2014 is the wrong citation here, I think Grossmann et al. 2013 is ok. Instead, see general comments above.

P. 3435, l.24 – P. 3536, l. 6: This paragraph needs to be rephrased as being confusing in the current form, i.e. first is stated that CHOCHO is not found, then sensitivity tests of O4 were performed but not further explained and the next sentence is again about CHOCHO (which was said to be not found before).

P. 3535, l. 7-12: I assume there was no shift and squeeze of Ring allowed because it is calculated from I0 (so the second Ring spectrum wasn't also allowed to shift)? In addition, was there a shift between I and I0 allowed overcoming wavelength shifts due to temperature instabilities of the spectrometer (and was the same shift applied to the rest of cross-sections)?

P. 3436, l. 13 ff: Why can the calculation of correction spectra for VRS be based on measured spectra? In measured spectra I expect that all effects (VRS etc.) are already included? So the result will be not as accurate as taking a solar atlas (see general comments above).

P. 3436, l. 15-16: "For weak absorbers, we can approximate the measured spectrum with the reference spectrum I0". I think one needs an initial spectrum that contains already strong absorptions from the stratosphere (as the inelastic scattering happens

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afterwards and these absorption lines can be filled-in similar to Fraunhofer lines) but not tropospheric absorptions which are "included" to the spectrum after the inelastic scattering event? If I'm right, please rephrase, if I'm wrong, please clarify.

P. 3437, l. 3-10: In Eq. 20, nominator and denominator are both based on a solar atlas and not measurements (because on P. 3436, l. 15-16 it is stated that the reference spectrum I0 can be used)?

P. 3437 Sect. 4.1 and Fig. 6: Can something be learned from the slope of these correlation lines (it is mentioned that phase functions differ and thus a linear slope is surprising as many different viewing geometries contribute to Fig. 6) → I would like to encourage a closer connection to Sect. 2 (cross references etc.).

P. 3438, l. 25 ff: For clarification, please write down the equation used here (between v , R and S) at first appearance (or refer to Eq. 21).

P. 3438, l. 28 to P. 3439: Why is only v_{Ring} expected to contain the VRS structures? According to Tab. 5 also a zeroth order intensity correction is included and Fig. 3 suggests large similarities between offset correction and VRS, so I would assume that also v_{offset} contains some of the VRS? And what about the second Ring cross section (λ^{-4})?

P. 3439, l. 20-21: Where do the vibrational and pseudo-vibration-rotational cross sections come from? I think the aim of Sect. 2 needs to be pointed out more clearly in the beginning because initially my expectation was that cross-sections of VRS are directly retrieved here from residuals.

P. 3442, Sect. 5.2: A recent study found a similar behavior for liq. water VRS impacts on NO2 slant columns (Peters et al, 2014), see general comments above.

P. 3443, l. 8: "...leads also leads..."

P. 3445, l. 6-8: This is a bit too ambitious as applying only to 2h averages (see general comments above). Please formulate more carefully.

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P. 3447, I. 22-24: Again too ambitious, if this sentence applies only to N2 and O2 VRS (but not liq. water VRS). The presence of N2 and O2 VRS is shown here in MAX-DOAS data, but not in satellite data.

P. 3448, first two paragraphs: This is important information which I think should be highlighted somewhere: 1) The two strong Ca lines produce strong Fraunhofer ghosts at 433 and 437 nm (IO fit range) which needs special compensation; and 2) “in spectral regions without large Fraunhofer ghost structures the offset polynomial . . . can compensate for most of this effect” (this is also in agreement with previous studies and of important information for practical use).

Fig. 2: I am confused by the x-axis label (certainly “wavelength” below the lowermost plot applies to all subplots) and the titles of subplots. I think the subplot titles provide no new information (as also given in the legends) and can be removed for cleanliness?

Fig. 2: How were these intensities calculated (please indicate equation number similar to Fig. 3). Was this calculated using DOASIS like the Ring compensation spectra?

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 3423, 2015.

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