

## 1 General Response

(Numbers of equations, figures, lines and pages refer to the discussion manuscript, if not mentioned otherwise. **Authors' reponses are written in bold face**, the referees' text is shown in normal face.)

**Before answering each comment in detail:** We decided to add another measurement campaign to the manuscript, in order to show that the effect of VRS( $N_2/O_2$ ) is not related to liquid water VRS. Nevertheless, we would like to emphasise, that even without an additional measurement campaign, the detection of VRS( $N_2/O_2$ ) from this campaign is unambiguous.

- The correction spectra for VRS of  $N_2$  and  $O_2$  which were found in our measurements had been calculated based on cross-subsections known from Raman spectroscopy.
- The reduction in RMS is correlated with the amount of inelastic scattering in the atmosphere, the magnitude of the Ring signal. As pointed out, for some random spectrum also a reduction of RMS can often be observed, however, a correlation with the amount of inelastic scattering would be just a coincidence.
- The magnitude of the fitted VRS ( $N_2/O_2$ ) signals is correlated with the magnitude of the Ring signal. The liquid water VRS would rather correlate with the light path under water.
- The ratio of both signals is in agreement with expectations from theoretical calculations.
- The intensities of VRS( $N_2/O_2$ ) and liquid water VRS show clearly different spectral structures (See Fig.2), in particular the liquid water VRS signal has a much broader spectral signature (in intensity space).

All these reasons show that vibrational raman scattering in the gas phase, which is expected from basic physics, is indeed found in passive DOAS measurements and also agrees quantitatively with theoretical expectations. These points are emphasized more clearly in the revised manuscript.

## 2 Response to Anonymous Referee #1

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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.

We would like to thank Referee #1 for his comments. Reading the comments helped a lot to understand how the manuscript was perceived and allowed us to determine which parts of the text need to be stressed and where additional explanations are needed.

## 2.1 General comments:

1. (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).

We point this out more clearly in the revised abstract. The spectral signature due to liquid water VRS is only stronger for certain viewing geometries and depends furthermore also on the turbidity of the water, as already pointed out in [Peters et al., 2014]. Additionally also the spectral signature differs significantly from those for VRS( $N_2/O_2$ ) due to the broader Raman response. However, in order to avoid confusion of VRS of  $N_2$  and  $O_2$  with VRS of liquid water, we agree that this needs to be mentioned already in the abstract, where it is now added.

2. (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 authors didnt 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  $N_2$  and  $O_2$  VRS in measurements over land in order to destroy these concerns (the authors briefly mention that they included but didnt successfully find a simulated liquid water VRS spectrum from Grossmann et al. 2013 which is not further discussed and in my eyes not sufficient).

As stated in the manuscript (e.g. at page 3427 line 16ff) and above, the Raman response of liquid water VRS is spectrally significantly broader and furthermore at a different energy/wavenumber as the one observed for gases, in this case  $N_2/O_2$ . In order to further clarify this important difference, figure 1 has been extended to encompass the liquid water Raman response, which is scaled arbitrarily. This is also already illustrated in Figure 2: The additional intensity due to liquid water VRS is a smooth function of the wavelength, since the liquid water Raman response is broad. Additionally, it is shifted about 20nm further to longer wavelengths than the additional intensity due to VRS of  $N_2$ . We reorganized some sentences in the introduction in order to clarify this difference.

The spectral structures due to VRS in liquid water are significantly different from those caused by VRS of  $N_2/O_2$ . To clarify the possible influence of liquid water absorption and VRS in liquid water, we added the respective detection limits for both effects and the correlation coefficient of  $R^2=0.03$

and  $p=0.1$  for the magnitude of both effects to the manuscript. To clarify this point even further, we added the analysis of another measurement campaign to the manuscript: During the MAD-CAT campaign at the MPIC in Mainz a comparison of MAX-DOAS measurements was performed. These data were initially not chosen for this publication due to the presence of large  $\text{NO}_2$  absorptions and significant glyoxal absorption. We added two figures to the manuscript: A spectral fit (now spectral fits from both campaigns are shown in Figure 5) and a correlation plot of the magnitude of the Ring effect and the magnitude of VRS for  $\text{N}_2$  (in analogy to Figure 6). The relative contribution of  $\text{VRS}(\text{N}_2)$  is in agreement with theoretical calculations of the cross-subsection and significantly contributes to the measured OD. The results are added to Table 6.

3. (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  $\text{N}_2$ , 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  $\text{N}_2$  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  $\text{N}_2$  and  $\text{O}_2$ . Is there any effect that prevents this structure to be shifted to approx. 430 nm for  $\text{N}_2$ ?

The increase of the sunlight spectrum at 400nm (compare figure 2, top panel) is shifted to 427 nm ( $\text{O}_2$ ) and 441 nm ( $\text{N}_2$ ) and consequently the Raman response also shows an increase. However, this increase is not as distinct as in the case of liquid water VRS due to two reasons: The  $\text{N}_2/\text{O}_2$  VRS cross-subsection scales with  $\tilde{\nu}^4$  (Eq.: 14), which compensates a part of this effect. Additionally also the strong Ca- Fraunhofer lines can be found at this wavelength, which introduces large differential structures in the Raman response for  $\text{N}_2$ . This makes it harder to identify this increase. For the case of liquid water the intensity increase is smoothed due to the broad Raman response of liquid water (as mentioned above). Fig. 5 is showing optical densities, not differential optical densities. The non-differential part is compensated in this case by a polynomial over wavelength (added explicitly to the revised manuscript). The convoluted cross-subsections are the absolute cross-subsections, they are not high-pass filtered to obtain their differential part. This is done implicitly by the DOAS polynomial included in the fit settings and is now stated explicitly in the revised manuscript.

4. (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.

**This is not the case, see point 2):** In order to illustrate this point further we added detection limits and a correlation coefficient for the obtained liquid water VRS signal and liquid water absorption to the manuscript. Even with a larger fit window (432-460 nm) absorptions due to liquid water and contributions of liquid water VRS could not be identified. Additionally, no clear relationship between liquid water absorption and liquid water VRS was found in the data from M91. We added a statement to this effect this to the spectral retrieval subsection in a subsubsection for M91 specific points in the revised manuscript.

5. (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  $I/I_0$ ). Is there really enough information that all these effects can be distinguished?

**Formally, the information content of the spectral data is clearly sufficient:** The fit range consisted in this case of 316 individual channels (M91). At a instrument function width of 6 channel, this results in about 52 degrees of freedom. The DOAS fit itself contains the following degrees of freedom: absorbers+pseudo absorbers (9), DOAS polynomial (3), intensity offset correction (1), shift and squeeze of absorption cross-subsection (2), in total 15 free variables, which need to be determined by the fit. Furthermore, the fit error is determined from the RMS and the inverse of the covariance matrix of all fitted spectra. The diagonal entries of the inverse of the covariance matrix will be large (theoretically infinite) for all cases in which the used cross-subsection spectra are not linearly independent, in other words: for cases in which the subspace created by them has not full rank. As seen from the results of the DOAS analysis (e.g. Figure 4), the fit errors are of reasonable size. As mentioned in the discussion part of the manuscript, the contribution from VRS( $O_2$ ) is small and in most cases negligible. A direct correction of the Ring spectrum seems straightforward, but has some shortcomings which are discussed in the manuscript on p3446 and 3447. In summary, we can conclude that there is really enough information in our spectra to distinguish these effects.

6. (5b) This isnt 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 subsection and (linear combinations of) Ring and VRS spectra. Did the authors check for this?

**As shown in Figure 6, the Ring effect signal and the signal of VRS correlate quite well, as expected from theory.** Time series of the magnitude of the Ring effect can e.g. be seen in [Wagner et al., 2009] or other publications

on the Ring effect in DOAS evaluations. The IO dSCDs however show a distinct separation of elevation angles as it is the case for any tropospheric absorber in MAX-DOAS measurements. A correlation of Ring and IO was not observed, IO dSCDs were also always positive within the respective measurement errors, as expected for a tropospheric absorber. Positive and negative Ring signals were found, depending on the observation geometry.

7. (5c) Maybe related: I heard DOAS people often state the matrix inversion will fail (or produce very large fit errors) if the cross subsections 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 subsections) 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?

**We are not sure whether the reviewer is referring to the DOAS fit itself or to the problem of inverting the (often) ill-posed problem of aerosol extinction or trace gas concentration height profile retrieval based on ground-based MAX-DOAS measurements. For DOAS fits this error is almost never seen. In a DOAS fit (unless you include two identical cross-subsections, or more cross-subsections than degrees of freedom of the spectrum / channels), a solution of the  $\chi^2$  minimization is found, by definition of the minimization problem. The cross-subsections (and the polynomial) do not have to be orthogonal, it is sufficient that they are linearly independent. The fit error calculation accounts for similarities in fitted cross-subsections, as mentioned in the answer to 5a).**

8. (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 in DOAS measurements. In particular:
9. (6a) Fig. 3 and P. 3427, l. 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.

**This is correct, and additionally to Richter et al. 2011, also Peters et al 2014 is now cited in this context.**

10. (6b) In contrast,  $N_2$  and  $O_2$  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?).

**This is correct: The constant contribution to observed intensities is, as the name already implies, completely compensated by the intensity offset correction. The contribution which is not compensated originates from the**

**Fraunhofer Ghosts.** We tried to mention this point again and more pronounced in the revised manuscript. The magnitude of liquid water VRS strongly depends on the viewing geometry.

11. (6c) The influence of VRS on  $\text{NO}_2$  slant columns is also in agreement with the mentioned paper but the difference is one order of magnitude smaller (most likely because  $\text{N}_2$  VRS is smaller than liq. water VRS) which can be mentioned.

The study by [Peters et al., 2014] during TransBrom was conducted over very clear ocean water, M91 took place in the biologically highly productive Peruvian upwelling. The influence on  $\text{NO}_2$  SCDs during TransBrom was only a magnitude larger for those measurements with elevation angles between  $0-1^\circ$ , i.e. with ocean water inside the field of view. These two effects share the same name, but their effects on the spectral retrieval do not necessarily have to be similar. As pointed out for IO, no significant change of dSCDs was observed for  $\text{VRS}(\text{N}_2/\text{O}_2)$ , while for VRS of liquid water an effect on IO dSCDs was identified in [Großmann et al., 2013]. We mention [Peters et al., 2014] and the impact of  $\text{VRS}(\text{liq. water})$  on  $\text{NO}_2$  dSCDs explicitly in the revised manuscript.

12. (6d) As here  $\text{N}_2$  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  $\text{N}_2$  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.

The conclusion that liquid water VRS cannot be detected in turbid coastal waters is also supported by [Peters et al., 2014] and [Dinter et al., 2015]. Based on the actual detection limits for liquid water and liquid water VRS (see comment 2), we agree with this conclusion and added it to the revised manuscript. In the Peruvian upwelling region the turbidity of the water is caused by high bio-productivity.

13. (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, IO, 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 means the measured reference spectrum IO, 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?

Maybe the confusion does not originate from the naming itself, but rather from the fact, that certain equations (especially Equation 21 as part of Equation 20) can be applied to both types of spectra: Modelled spectra based on a solar atlas and measured spectra. Both spectra represent an extreme case for the incoming radiation: One does not show any filling in of Fraunhofer lines, while the other shows the maximum possible filling-in. Both are not correctly representing a scattering process occurring somewhere in the atmosphere, since the actual amount of filling-in will be found in between those two extreme cases. This problem could be solved by explicitly implementing VRS( $N_2/O_2$ ) in a radiative transfer model. The filling in due to RRS however is typically below 2%: The filling-in due to VRS( $N_2$ ) is of the order of 0.04%, therefore the resulting differences for the VRS( $N_2$ ) correction spectrum are of the order of  $8e-6$  and therefore not significant for current DOAS applications. If this accuracy is however needed, radiative transfer modelling similar to existing studies on rotational Raman scattering (e.g. [Rozanov and Vountas, 2014]) is indeed necessary. This estimate was added to the revised manuscript. We added additionally a table with the list of variables.

14. (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-subsections in single measurements of several seconds integration time where it is practically not detectable but might introduce interferences with other cross-subsections. 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.

We rephrased the first sentences of the conclusions, including estimates of the change in RMS as found in subsection 5.1. We added a sentence that VRRS could not be identified in measurement data due to too large RMS of the measurements and the similarity of the resulting intensity offset due to VRRS with the general intensity offset correction (mentioned on page 3440 line 1-3 of the discussion manuscript).

15. (9) It would be a benefit if the authors could provide a table with their  $N_2$  VRS spectrum (in 0.1 nm resolution it shouldnt be a too big table; maybe it can be provided also in the supplement).

This is done, based on the Kurucz2010 solar atlas. However, it is not a simple spectrum, since division and convolution do no commute and the

ratio of the convoluted additional intensity and the convoluted solar atlas depends on the actual slit function of the respective instrument. We used the total cross-section averaged over the complete solid angle (given in the manuscript, now equation 14 in the revised manuscript) in order to give it in units of  $\text{cm}^2/\text{molec.}$

## 2.2 Specific comments:

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

**This information was added to the abstract.**

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

**This was added to the abstract.**

3. 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) .

**In the first part of the sentence we already wrote: 'Consequences of VRS are red-shifted Fraunhofer structures in scattered light spectra'. In order to clarify the red-shift, we added the magnitude of the spectral shift in the revised manuscript.**

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

**Thats true, it was added to the list in the revised manuscript. However, inelastic scattering plays no significant role there as reported by [Cede et al., 2006]**

5. P. 3425, l. 7: The MAX-DOAS principle allows to reach higher sensitivity ::: This doesnt somehow fit to the sentence before where you already mentioned off-axis measurements. Maybe this could be rephrased.

**We rephrased the sentence.**

6. P. 3425, l.14: ::: in particular narrow lines ::: doesnt 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)?

**If the width of the Fraunhofer line is broader than the width of the shift due to RRS, then the filling-in is not that strong in the middle of the Fraunhofer line.**

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

**It took us a while to find the translated manuscript, but this reference ([Shefov, 1959]) has now been added to the revised manuscript.**

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

**We changed all forms to filling-in.**



9. P. 3426, l.21: Isn't there also a mode around 1600  $\text{cm}^{-1}$  for water vapour (see above)?

There is an additional mode at 1650  $\text{cm}^{-1}$  and 2100  $\text{cm}^{-1}$  for liquid water VRS, but its size is only about 1/5 of the Raman cross-section around 3400  $\text{cm}^{-1}$ . [Schmidt and Miki, 2007]. This information was added to the revised manuscript. Water vapour shows only a strong Raman response at 3654  $\text{cm}^{-1}$  according to [Penney and Lapp, 1976] (this citation was confused with [Penney et al., 1974] in the original manuscript and was corrected).

10. 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  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , 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.

1. We added an introductory sentence to this paragraph in order to clarify that we are here indeed referring to intensities. Later on, it is explained how this translates to optical densities in common DOAS evaluations. 2. Yes, indeed. We added the liquid water Raman response also to Figure 1 as mentioned already on page 3427 in line 16ff to further illustrate this point. In the discussion manuscript this was also shown in Figure 2.

11. 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  $\text{N}_2$  VRRS be somewhat smeared as well?

Well observed. For this reason the intensity due to VRRS in Figure 2 is as smooth as the intensity caused by RRS. This is now explicitly noted in the revised manuscript: '*A 'blurred' remapping of the solar spectrum is also observed for RRS and VRRS of  $\text{N}_2$  and  $\text{O}_2$ , since the respective cross-sections consist of several lines separated by only a few  $\text{cm}^{-1}$ , which are not separated in typical DOAS measurements.*'

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

This is already explicitly mentioned on page 3427 line 16ff.

13. 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)?

It is implicitly assumed that the lightpath is the same for RRS and VRS scattered light, since the mean free path associated with both processes is significantly larger than the scale height of the atmosphere or typical light-path lengths. The effective lightpath is thus not significantly altered by VRS. Since later on the ratio of both processes is compared to the expectations from theory, the absolute length of the light path does not matter. This statement was added explicitly to the revised manuscript.

14. 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).

**It is stated already in the first manuscript on page 3429 in line 2: *Note that the term differential refers here to the solid angle.***

15. 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?

**There does not appear to be a unique use of these terms in the literature, we nevertheless changed it accordingly.**

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

**Or by applying another filter method. We mention now in the revised manuscript, that a polynomial is fitted together with the trace gases to the measured OD.**

17. 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).

**This is correct and equation 17 implicitly containing the SCD was changed in the revised manuscript to account for non-constant concentration profiles. The term SCD had been already introduced in the manuscript on p3433 in line 6.**

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

**All elevation angles were corrected for movements along the 'roll'-axis of the ship. However, since it was a 1D-telescope, the correction took only place in the plane of the elevation angles and was therefore only partly compensating the ships pitch movement for larger elevation angles. However, for these elevation angles the sensitivity of MAX-DOAS measurements to small elevation angle offsets is significantly smaller than for lower elevation angles.**

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

**The name slit function is now also mentioned in this context.**

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

**The stability of the instrument (M91) was tested by a spectral evaluation against a fixed reference. The shift of the reference spectrum showed then the maximum shift due to instrumental instabilities, which was less than 0.01nm within a day. This information is now added to the revised manuscript. We also added this information for the newly added measured MAD-CAT campaign.**

21. P. 3434, l. 13: Why 40 elevation and not a zenith spectrum as reference  $I_0$ ? The absorption signal of tropospheric absorbers in measured OD will be larger then.

Due to the encountered SZAs of less than  $5^\circ$  and thus the possibility that in the southern part of the cruise zenith sky spectra might be affected by direct sun light,  $40^\circ$  elevation spectra were chosen as reference spectra. Since the main information is obtained from the ratio of the Ring and VRS signal, the choice of the elevation sequence Fraunhofer reference does not change the overall result.

22. 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 ships course changed from time to time. If such a change occurs within the average of 16 sequences the viewing azimuth changes dramatically.

**We are aware that the ship (and the sun) were moving. However, since a reduction of RMS was observed when co-adding 16 elevation sequences and it yielded still some time resolution, this allowed to show the effect of VRS more clearly in a DOAS fit. (See also answer 1.2 to referee #2). The effective time resolution was about two hours and is already mentioned in the manuscript.**

23. 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?

**The first Ring spectrum is not normalized, but is calculated according to Eq (1) for 0.8 N<sub>2</sub> and 0.2 O<sub>2</sub> molecules. Therefore the number given for the Ring signal magnitude is also given in molec/cm<sup>2</sup>. About the second Ring spectrum: See answer 2.12 to referee #2**

24. 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.

**Thats true, [Peters et al., 2014] did not discuss this, however, [Peters, 2013] did. This is corrected.**

25. 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).

**These sentences are reorganized. The sensitivity study was done for glyoxal, using different O4 literature cross-subsections. A table with an overview of the fit settings for each species is added.**

26. 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 wasnt 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-subsections)?

**The Fraunhofer reference spectrum was chosen from the same elevation sequence, therefore its shift was typically smaller than 1pm, even when it was**

not fixed to zero. Here it was fixed to zero. To account for possible temperature instabilities of the spectrometer, the literature cross-subsections were allowed to shift relative to the measured spectra and the spectra calculated from the measured spectra (1/I0, Ring, Ring4). Note that in DOASIS the measurement spectrum is always fixed and cannot be shifted. In other DOAS software, the measurement spectrum can be shifted, but then the literature cross-subsections are not shifted. We added a table to show the dependencies on different fit settings with respect to shift and squeeze for the M91 data set.

27. 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).

**See answer to comment 13 above.**

28. 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 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 Im right, please rephrase, if Im wrong, please clarify

**In reality, that is true. We did this approximation in the beginning of the paragraph, in order to simplify the Taylor expansion in (19). This approximation is (when the stray light correction term  $1/I_0$  is used, or a Ring correction spectrum is used) otherwise needed in the end of the argumentation, because the Taylor expansion for  $\ln(I + J_i)/I_0 - \ln(I/I_0)$  yields  $J_i/I$ , which can then be approximated in the case of weak absorption by  $J_i/I_0$ . We reorganized this paragraph in order to clarify this.**

29. 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)?

**As stated in answer to major point 5a), this calculation can be used for both, a measured spectrum as well as for a spectrum based on a solar atlas, since its just a Taylor expansion term of an additional intensity in the calculation of the optical depth.**

30. 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.).

**As described on page 3438 in line 6 the relative sizes of the cross-subsections of VRS and RRS are determined from this correlation plot. In fact, the non-isotropic phase function of RRS disturbs this correlation theoretically, but (as stated on page 3447 line 1ff), no significant dependence on the scattering angle could be found for the observations, probably this effect is not visible**

due to the measurement error, which is of similar size. We extended the discussion of the results in the revised manuscript.

31. 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).

**We added a cross-reference to equation 21.**

32. 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 subsection ( $\lambda-4$ )?

**As we did not find any VRS-like structures in  $v_{offset}$ , we assumed that the magnitude of the offset is dominated other effects, such as instrumental straylight. Its magnitude is not expected to correlate with the light-path length as it is the case for RRS and VRS, but rather with the relative intensity of the measured spectrum and other spectral ranges outside the measured wavelength range. As the second Ring cross-subsection is a correction to the original Ring, it was not included in the regression analysis. This was clarified in the revised manuscript.**

33. P. 3439, l. 20-21: Where do the vibrational and pseudo-vibration-rotational cross subsections 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-subsections of VRS are directly retrieved here from residuals.

**The pseudo cross-subsection for VRS( $N_2/O_2$ ) have been calculated according to equation 21, as it was already the case for Figure 4. This is now stated more clearly. A direct retrieval of the VRS structure is impossible, since the 'correct' dSCDs of all other absorbers, which might compensate for a part of its contribution, are also not known beforehand.**

34. P. 3442, Sect. 5.2: A recent study found a similar behavior for liq. water VRS impacts on  $NO_2$  slant columns (Peters et al, 2014), see general comments above.

**See answer to 6c), this was added to the manuscript.**

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

**Thank you, this sentence was corrected.**

36. 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.

**A RMS criterion was added to this sentence, as explained in subsection 5.1.**

37. P. 3447, l. 22-24: Again too ambitious, if this sentence applies only to  $N_2$  and  $O_2$  VRS (but not liq. water VRS). The presence of  $N_2$  and  $O_2$  VRS is shown here in MAX-DOAS data, but not in satellite data.

**We rephrase the sentence: Vibrational Raman scattering of  $N_2$  and  $O_2$  can contribute significantly to observed optical densities in passive DOAS applications. This was shown for ground-based and ship-based MAX-DOAS**

observations and is expected to contribute in the same amount to other passive DOAS techniques, such as airborne or satellite measurements.

38. 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).

**We rephrased the first sentences of the conclusions in order to highlight these points more.**

39. 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?

**Thank you for this suggestions, the plot was updated in order to provide more space for the actual information content.**

40. 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?

**The intensities were calculated according to equation 13. We updated the cross-reference in Figure 1.**

### 3 Response to Anonymous Referee #2

Received and published: 27 April 2015

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 N<sub>2</sub> and O<sub>2</sub> 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:

**We would like to thank Referee #2 for his comments. We considered his major comments, his observations and his minor comments in the revised manuscript. The detailed comments helped to understand the way in which the manuscript was perceived by the reader.**

#### 3.1 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 be addressed in the retrieval of NO<sub>2</sub>, IO, glyoxal (CHOCHO), and water vapor (H<sub>2</sub>O). 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. (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 subsection 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).

If some other cross-subsection is added to the fit, a reduction of RMS is typically expected. However, a correlation of this reduction with the amount of inelastic scattering is not expected, but is found here. This shows, that the Ring spectrum only incompletely models the effect of inelastic scattering in the atmosphere. VRS of  $N_2$  and  $O_2$  is a potential candidate to explain this discrepancy.

The fact that IO and Glyoxal dSCDs are not significantly affected by this additional apparent optical density due to VRS of  $N_2$  and  $O_2$  observed in measurements was not expected because the ODs of IO and Glyoxal and VRS( $N_2/O_2$ ) are of the same order of magnitude for measurements in the remote marine boundary layer (e.g. [Großmann et al., 2013, Mahajan et al., 2014]) and polar regions (e.g. [Frieß et al., 2010]) and it was not investigated before. Furthermore it depends on instrumental parameters, as e.g. the spectral resolution of the spectrometer (p3441 l27).

Even more important is the fact that the RMS and thus also the detection limits can be reduced, as indicated at the beginning of subsection 5. This is e.g. important for measurements in the pristine remote marine boundary layer or in polar regions. We also stated in subsection 5.1 that, if this effect is not considered, for large Ring signals no fits with an RMS below  $5 \times 10^{-5}$  are possible. Already a an RMS of  $1 \times 10^{-4}$ , the residual structures due to VRS of  $N_2$  will be clearly visible. In order to exclude the possibility of cross-talk to liquid water VRS, we decided to add another measurement campaign to this manuscript to show the effect of VRS in a different environment. Since the number of our land-based measurement campaigns with good MAX-DOAS instruments in non-polluted regions without water or ice (which can also show spectral signatures according to its Raman cross-subsection) is limited, we chose a data-set from the MAD-CAT campaign, despite large  $NO_2$  absorption and significant glyoxal absorption.

2. (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.

(We assume that you meant the opposite in the first sentence.) The effect of VRS is important whenever the residuals are of comparable size, typically around  $10^{-4}$ , as pointed out at the beginning of subsection 5, and the measurement geometry is such, that filling-in of Fraunhofer lines is observed (Ring-effect) relative to the respective Fraunhofer reference. At this order of magnitude of the RMS, measurements are often photon shot noise limited (see e.g. also Coburn2013). Since for photon shot noise a scaling of the RMS with  $\sqrt{n}$  is expected, this was tested by co-adding elevation sequences to reduce the overall RMS: Plotting the RMS versus intensity on a log-log scale, a so called Allan-plot, allows to estimate at which RMS photon shot noise dominates and where systematic residual structures start to contribute significantly. We added a statement explaining this to the revised manuscript. A number of 16 elevation sequences was chosen as a compromise between acceptable time resolution and low RMS, which was clearly not any more photon shot noise dominated. This can be seen from the structured fit residual in Figure 5, which is not dominated by Gaussian noise any more. We are here therefore by definition at the limit of the current spectral evaluation.

3. (3) The current DOAS analysis considers quite a lot of manipulation, for example, two rings are fitted all cross subsections 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 N2/O2 VRS I suggest to clearly perform a thorough analysis of cross-talk of the VRS with several DOAS settings.

These effects had been investigated before and have now been added to the manuscript as an additional table. The details on which cross-subsections have been shifted and squeezed have been clarified: Ring spectra and Fraunhofer Reference are not shifted, all cross-subsections are shifted simultaneously relative to the measurement (and thus also the Ring-) spectrum to compensate for instrumental instabilities. This shift is determined from a fit of the measurement spectrum to a solar atlas. Upper limits for the spectral stability of the instruments were added to the revised manuscript.

4. (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.

A RMS of  $2 \times 10^{-4}$  can be obtained with usual MAX-DOAS instrument (as used here) based on spectra recorded for one minute. A time resolution of two hours (corresponding to an exposure time of 16 minutes for M91) was chosen here to reduce the overall noise and to highlight the effect of VRS. Such small residuals are needed in cases in which the detected trace-gas



dSCDs are close to their respective detection limit. For these applications often the time resolution is not as important, as the successful detection or the successful reduction of the trace gases detection limit. For the case of IO, this is the case for the remote marine boundary layer and for investigations of its abundance in polar regions.

5. (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).

(1) We added additional subsections, restructured especially subsection 2 and added more introductory sentences at the start of subsections in order to clarify the intent of the respective description: At p3434 l11 e.g. we added an introduction to the spectral retrieval in order to clarify the goals of the analysis. (2) We added definitions of missing acronyms and we added information about the co-adding of spectra, as described in answer 2.

6. (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.

We intended this publication as a discussion of an additional contribution to the Ring effect, which has so far not been considered in spectral DOAS evaluations. We showed that the VRS signal is directly correlated with the Ring signal, as it is expected theoretically, and that it can contribute significantly to measured optical depths. Phase function differences could not be clearly detected due to limits of detection (p3447 l6-7). For diurnal variation of the Ring signal for MAX-DOAS observations, other publications (e.g. [Wagner et al., 2009]) are available.

The effect of VRS has a long mean free path due to its small absolute cross-section. When the mean free path due to Rayleigh extinction is around 20km, the mean free path of Rotational Raman scattering is 50 times larger (around 1000km) and the mean free path of VRS even 2500 times larger. It is therefore reasonable to assume that a photon is typically not scattered twice due to RRS, VRS or even VRRS. (compare also Table 6 for cross-section values) As current radiative transfer models typically neglect VRS(N<sub>2</sub>/O<sub>2</sub>) (see e.g. LIDORT ([Spurr, 2008]), SCIATRAN ([Rozanov and Vountas, 2014]), McArtim ([Deutschmann et al., 2011]) ), a discussion is difficult. An implementation in a RTM for VRS(O<sub>2</sub>/N<sub>2</sub>) would be however useful to investigate the effects of the phase function further, but due to the long mean free path, geometric considerations could be sufficient. As mentioned on p3447 l6-7, it could however not be detected in measurement data, most probably due to too large fit errors.

### 3.2 Specific observations:

1. 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 abstract 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.

**We extended the description of the approach to detect VRS in the abstract. We did not include specific results for various trace gases, which have been observed in significant amounts during the cruise ( $\text{NO}_2$ ,  $\text{BrO}$ ,  $\text{HONO}$ ,  $\text{HCHO}$ ,  $\text{IO}$ ,  $\text{O}_4$ ,  $\text{H}_2\text{O}$ ), since this is not our main focus of this manuscript and the interpretation of their abundances would be a different topic. VRS of  $\text{N}_2$  and  $\text{O}_2$  is a contribution to all passive DOAS measurements and does not only apply to this specific cruise.**

2. 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,  $\text{OClO}$ , and  $\text{BrO}$ , and not  $\text{IO}$ ,  $\text{CHOCHO}$  that are the gases you are presenting results.

**We modified this list in the revised manuscript. Absorbers in the UV can however also be affected by VRS of  $\text{N}_2/\text{O}_2$ , as discussed on page 3444 subsection 5.2. A (good) quantification from measurements in this region was however not possible, due to overlaying dominating residual structures which are not correlated with the Ring signal as mentioned on page 3444 line 12ff subsection 5.2.**

3. 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.

**In the introduction we now introduced the trace-gases also with their full names and their respective formulas. However, we kept e.g.  $\text{NO}_2$  as well as glyoxal, as this seems to be easier to read (in case of  $\text{NO}_2$ ) and/or easier to pronounce (glyoxal).**

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

**We corrected the revised manuscript accordingly.**

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

**This figure was calculated based on Equation (1), summed over all molecular eigenstates. Eq (13) is showing the sum over all states of the molecule, including its respective weighting. This cross-reference is now explicitly stated in the revised manuscript.**

6. 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 subsections of Fig 1, and the cross subsection magnitude given in the text it should be 50-100 times higher. Please clarify.

**Here, the water vapour VRS cross-subsection was compared to the VRS ( $\Delta J = 0; \Delta \nu = 1$ ) cross-subsection. Figure 1 shows the individual contributions for different rotational eigenstates of the molecule, and the VRRS ( $\Delta J \neq 0; \Delta \nu = 1$ ) transitions are indeed individually two orders of magnitude smaller. The cross-subsections values, individually for VRS and integrated over all possible transitions for VRRS, see Table 6 of the discussion manuscript.**

7. Page 5, lines 5-15: The quantitative description in subsection 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.

**We agree with this comment and reorganized the structure of this paragraph to improve readability. Additionally the subsection was subdivided into subsubsections.**

8. 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 Maxwells equations for scattering of spherical particles. In short, the extinction is not caused by Mie. I would not call Mie and Rayleigh extinction, instead use extinction from particles and molecules.

**We rephrased this sentence to : 'To remove broad-band extinction from particles and molecules, the OD is subdivided...'**

9. Page 12, line 13: Is there a technical reason of using  $40^\circ$  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.

**The  $40^\circ$  spectra were chosen as Fraunhofer Reference spectra (for M91) in order to avoid direct sunlight at the  $90^\circ$  measurements. This could have been possible at noon for the southern part of the cruise track together with deviations of the elevation due to ship movements. Since the analysis is using the relative contribution of VRS to the filling-in of Fraunhofer lines by RRS, the choice of reference spectrum within an elevation sequence does not matter. We explained this now explicitly in the revised manuscript.**

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

**This is indeed true and we have removed equation 18 in the revised manuscript.**

11. Page 12, subsection 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?

The primary focus of this paper is the identification of the impact of VRS on MAX-DOAS measurements and its comparison to theoretically expected values. We added that the fit interval was aiming at detection of the VRS scattered light, therefore the region where the most pronounced Fraunhofer ghosts are expected was chosen. Impacts on retrieved trace-gases are a secondary focus. We chose a spectral range containing 430-440 nm, as Fraunhofer ghosts of the most prominent Fraunhofer lines at 393 and 396 nm are expected here. This is now explicitly mentioned in the revised manuscript. The Allan plot based on measurement data as described in comment 1.2) shows a reduction of RMS when adding 16 elevation sequences. When adding more elevation sequences, no further improvement was observed. If the residual of an individual spectrum already would have been dominated by systematic structures, a reduction of RMS by co-adding is not expected.

12. 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?

The second ring compensates for additional Ring structures which appear with a changing colour index (ratio between short- and longwave intensity), i.e. due to particle scattering. The first Ring is calculated according to equation (1) and (19). However, if in equation (19) the colour index of the spectrum in the denominator changes (e.g. due to scattering on particles), this translates directly to the Ring correction spectrum. The second Ring spectrum compensates this effect. The spectrum was not explicitly orthogonalized, but as it is calculated by multiplication of the original Ring spectrum by  $(\lambda^4/\lambda_0^4 - 1)$ , it only accounts for changes relative to the original Ring spectrum. Compared to orthogonalization, this procedure has the advantage that it does not change the contribution of the original Ring spectrum at  $\lambda_0$  by construction. We added this to the revised manuscript. Note that orthogonalization does not change the nature of the minimization problem which has to be solved, it is just another linear combination of the same cross-subsections used in the fit. It might however help to improve the numerical stability of the fitting procedure.

13. 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?.

Yes, as supported by comparison of the 404nm line to the line at 407nm and the red half of the dominating emission line at 435nm. A fit using a Gaussian instrument model function showed a variation in the slit function width from 404-435nm of less than 2.5% for both campaigns. There are no strong absorbers in the spectral range we analyse (most water vapour absorptions are outside this range,  $\text{NO}_2$  is small for M91 and partly filtered for MAD-CAT) and a current Fraunhofer reference is used. Therefore the impact of

the wavelength dependence of the instrument slit function is minimized. A parametrisation by a Gaussian function with a wavelength dependent width would have also introduced uncertainties, since the slit function shape of both spectrometers is not exactly of Gaussian shape. We added error estimates for the wavelength change in slit function for the case of large NO<sub>2</sub> absorption of  $5 \times 10^{16}$  molec cm<sup>-2</sup>.

14. Page 13, lines 7-12: Describe what wavelength you are interested first, then explain why O<sub>3</sub> 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 N<sub>2</sub>/O<sub>2</sub> VRS?

We thank the reviewer for pointing this out, it was changed in the revised manuscript. The intensity offset correction was not found to correlate with N<sub>2</sub>/O<sub>2</sub> VRS, since the intensity offset correction is most probably dominated by other effects, as e.g. instrumental straylight from the infrared or other spectral regions. The explanation for the intensity offset correction can be found on page 3436 lines 21-24 of the initial manuscript.

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

The fit window range was mentioned in the initial manuscript on page 3435 (13) in line 27. We added Table 5 to the revised manuscript in order to clarify the DOAS retrieval settings for each effect or trace-gas.

16. 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?

We chose this wavelength window for the detection of VRS, not as a fit window for Glyoxal. The fit wavelength interval was mentioned on page 3435 (13) in line 27, where the upper limits were determined. Since glyoxal is not the focus of this manuscript, but it could be a 'significant absorber' in the blue wavelength range, its upper limits were determined to exclude its interference with the detection of VRS (N<sub>2</sub>/O<sub>2</sub>).

We added a sentence in the beginning of the paragraph to clarify the aim of this discussion: *'Glyoxal shows absorption structures in the spectral range which is can be affected by VRS. It could therefore interfere in the spectral retrieval of the VRS(N<sub>2</sub>/O<sub>2</sub>) signal.'*

17. Page 12, lines: 7-12. It is mentioned that shift and squeeze are used for all the cross subsections (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.

**See answer to major point 3).**

18. 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?

**It was mentioned that the rotational constant of N<sub>2</sub>/O<sub>2</sub> does not change significantly (for DOAS applications) with the vibrational excitation state of the molecule. Therefore the approximation that the VRRS spectrum can be calculated as a shifted RRS spectrum can be applied. A reference for DOASIS and the ring calculation are given in the original manuscript page 3434 line 26. The calculations of DOASIS agree with equation (1) when only calculating it for rotational transitions.**

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

**We removed this part and rephrased this sentence, also in order to clarify that modelled spectra based on a solar atlas as well as measured spectra can be used to calculate the correction spectra (as mentioned already in the discussion).**

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

**This was changed in the revised manuscript.**

21. 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.

**The intensity offset itself is explained in Equation 18 and the following lines. We rephrased the sentence also in accordance with the reply to comment 2.32 from referee 1.**

22. Page 17, lines 24-25: The sentence: In other vectors corresponding to other absorbers or parameters the structure associated with N<sub>2</sub>=O<sub>2</sub>-VRS was not found. Is not clear. Do you mean that the VRS was important for some spectra and not for other?

**We meant by this sentence, that no spectra which correlated with the dSCDs of the other, respective absorbers and parameters showed a significant contribution from a VRS(N<sub>2</sub>/O<sub>2</sub>) spectrum. We write now: *'In other vectors corresponding to other absorbers or parameters a significant contribution of the structure associated with VRS(N<sub>2</sub>/O<sub>2</sub>) was not found. The vector corresponding to the intensity offset correction could have contained some contribution of VRS(N<sub>2</sub>/O<sub>2</sub>), as a part of it can be compensated by the intensity offset correction, however, no correlation of the magnitude of intensity offset correction and Ring signal was observed. We assume that***

*the intensity offset correction is mainly affected by instrumental straylight, which is e.g. depending on the colour index of the measured spectrum.'*

23. 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  $d()/d$  was calculated. Do you have to use Mie theory?

**We extended the description of how the values for the integrated cross-subsection values in Table 6 were calculated (summing over the respective transitions in equation 13). Table 6 contains already the two extreme cases of the phase function given in equation 11 and 12.**

24. Page 20, line 8: leads is mentioned twice.

**This was corrected in the revised manuscript.**

25. Page 20, lines 7-9: According with the sentence here the analysis of  $\text{NO}_2$  in the wave length range of 432-460 nm leads to an underestimation of  $\text{NO}_2$ , however I do not see how this was concluded, please expand this description. Also, when comparing the  $\text{NO}_2$  dSCDs the wavelength dependence should be considered, is this considered here?. I suggest to present quantitatively comparison of the  $\text{NO}_2$  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).

**The effect on  $\text{NO}_2$  dSCDs was separately compared with and without the correction for the contribution of VRS in each of the fit intervals. Therefore the dSCD wavelength dependence does not play a significant role here. It is estimated that the resulting mean difference from the two comparisons in different wavelength windows is affected by the wavelength dependence by maximally 10%, which clearly below the detection limit. We clarified this in the revised manuscript in the introduction to the evaluation of the impact of VRS on trace gases: '*For each comparison the same retrieval settings and intervals were used, once without and once with the correction for VRS of  $\text{N}_2$  and  $\text{O}_2$ .*'**

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

**The unit of the measurement spectrum is given in counts (as can be seen from Figure 5), thus also the intensity offset correction is given in counts according to equation 18. This is explicitly stated now in the figure's caption.**

27. Figure 9: how is the x-axis calculated?. I understand it as the  $\text{NO}_2$  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.

**The black lines are gauss-fits to each of the histograms. This was added as an additional sentence to the figure's caption in the revised manuscript. The effect on  $\text{NO}_2$  dSCDs was compared with and without the correction for the**

contribution of VRS in the given fit interval, which is now also mentioned in the figure’s caption.

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