Answers to Anonymous Referee 1:

General Comments

The manuscript entitled "Liquid water absorption and scattering effects in DOAS retrievals over oceans“ by Peters et al. describes ship borne measurements of aqueousvibrational Raman scattering and liquid water absorption structure. It has been shownby the authors that the retrieved spectral signatures of liquid water significantly improvethe DOAS retrieval, in particular for nadir-looking satellite (and probably also airborne)measurements, but also for ground-based observations if all or parts of the observedlight has been scattered by liquid water. Therefore the topic of this paper is of generalimportance for the UV/Vis spectroscopic community and well suited for a publication inAMT.
The methodological approaches appear to be valid. In particular, the retrieval of spectral structures of water by separating measurements with short integration time pointing on clear water and white caps is in my opinion an excellent idea since any structures from atmospheric trace gases or aerosols automatically cancel out. However, as detailed below there are several technical and language-related issues which should be resolved before final publication in AMT.
We thank the referee for the general positive comments and the thorough review which helped to improve the manuscript. We consider the technical and language related issues as well as the specific comments point by point in the following.

Large parts of this study rely on model calculations of the impact of liquid water on radiation using the SCIATRAN radiative transfer model. Although this has already been published elsewhere, I think it is very important for the reader to have some knowledge on how these simulations were actually performed. A short section describing the methods for the simulation of the spectral structures of liquid water should therefore be added.
In the revised manuscript we included a subsection about the performed SCIATRAN simulation. Please be also referred to our answer on Referee 2’s comment concerning P.5044, L.19.

In order to assess the improvement of the DOAS analysis using the retrieved spectral structures of water, relative changes in residual RMS for different fit scenarios are discussed. For the ship-borne measurements mean values of these changes are reported, whereas for OMI satellite measurements maximum values are listed. First of all, it is not possible to compare these two values. Secondly, a maximum value of a large dataset is not meaningful at all because it might represent an outlier. For these reasons I strongly recommend to report mean values of the relative change in residual RMS for the satellite observations as well.
We agree with the Reviewer. In the revised manuscript we therefore provide mean values also for satellite retrievals in 3 specified regions: (a) in the region where the TransBrom campaign was carried out, (b) in a large oceanic region of very clear water (tropical western Pacific, lat 0°-30° N and 130°-180° E), and (c) global means.

Specific Comments

5028.6: I do not think that the term “hyperspectral” is appropriate here, since hyperspectral imaging refers to imaging techniques, for which each pixel contains spectral information. The measurements described here, however, deal with spectroscopic measurements along a single line of sight and therefore not hyperspectral.

We agree that the term “hyperspectral” might be misleading. We therefore either deleted it or changed it for example to “< 1 nm resolution”.

5028.19 and 5028.24: Specify what you mean with “values of improvement” and “fit quality improvements” (i.e., decrease in residual RMS).

Yes, we meant “decrease in residual RMS”. We changed the formulation as suggested.

5030.7: I do not really understand why the absorption of radiation by particles in the water body should lead to a decrease in the filling-in of Fraunhofer lines by VRS. Actually, the strength of the filling-in is determined by the amount of Raman-scattered light relative to the total observed intensity, and both are equally affected by absorption. Therefore there should be no direct impact of absorption on the filling-in, except for subtle changes in the average light path.

This would be true if the entire light path was under water (as it was nearly achieved by our MAX-DOAS observations in this study). In contrast, the intensity measured by a satellite has many contributions:

$I_{TOA} = I_{atmosphere} + I_{surface} + I_{ocean}$

and the filling-in observed by the satellite depends on the relation of these contributions. VRS occurs in the water and an increased absorption in the ocean reduces this contribution relative to the others, i.e. VRS decreases in I_TOA if I_ocean decreases.

5031.23: I suppose that not only salinity, but also impurities have an impact on the apparent water absorption spectrum.

This sentence has been removed in response to a comment from Referee 2.

5031.29: I cannot see why the retrieved H_2O_{res}spectrum should be “hyperspectral”.

We changed that (see above)

5032.5: Please specify what you mean with “The H_2O_{res}spectrum was tested…” What kind of tests did you perform?

The meaning of that sentence is, that it was included (for test purposes) in satellite DOAS fits. We replaced that sentence by “In addition, the H_2O_{res} spectrum was included in satellite DOAS fits and successfully found over the clear ocean.”

Section 3.1: In its present form, equation 3 does not follow from equation 2. I therefore recommend to use the integral form of the Beer-Lambert Law (i.e., […] in the exponent of equation 2, and also to include terms for scattering by air molecules and aerosols. Then you could later (5035.25) explain that for liquid water rho is nearly constant along the light path, and equation 3 would directly follow from equation 2. Furthermore, only the density of water is nearly constant along the light path, but other constituents (impurities, organic compounds, algae, etc.) are not necessarily homogeneously distributed but also affect the radiative transfer and therefore, strictly speaking, need to be considered in Equation 2.

We changed the equation (and surrounding text) to the integral form and included terms for Rayleigh, Mie, and atmospheric Ring effect. For liquid water we included terms for

absorption and VRS. The referee is right, there might be additional effects that we neglect here for better readability (also the water during TransBrom was very clear as stated in the paper and we found no similarity of our retrieved spectrum and other constituents, e.g. chlorophyll).

5036.4: "This leads to the DOAS equation" – it is not clear what leads to this equation, as this statement certainly does not refer to the previous sentence. After modification of equation 2 as proposed above, you could simply state that the DOAS equation follows from equation 2, with the polynomial accounting for the broad-band component due to Rayleigh and Mie scattering.
Changed (see last comment).

5036.25: The chisquarenormalised by the number of spectral points is not equal to the RMS, but its square is: […]
Thank you, we corrected this!

5037.7: You mention the dark current as a possible source for an intensity offset. Didn't you remove the dark current prior to the analysis? In this case, it should not cause an offset except if there are temporal variations of the dark current, e.g. due to an unstable detector temperature.
Yes, we correct for the dark current. We address here exactly the point mentioned by the referee and therefore changed the text to "These intensity offsets can be caused by different effects, e.g. changes in the detector's dark current".

5038.6: Usually, the Ring effect refers to the impact of rotational Raman scattering on skylight. Here your state that vibrational Raman scattering is responsible for the Ring effect. Furthermore, it is not clear whether this sentence refers to scattering in the atmosphere or in the water body.
We agree that this sentence is a bit confusing and not very precise. The reason is that both RRS in the atmosphere as well as VRS in water lead to an in-filling of Fraunhofer lines (as explained in Sect. 2). We changed the text to make it more precise.

Section 3.6: It is not well explained how spectra representative for white caps and for undisturbed water were created. If I understand it right, you stored each 100 ms scan as an individual spectrum and afterwards averaged over spectra which you classified as "white caps" and "clean water". Furthermore, you should mention the important aspect that, by looking at the ratio between white caps and clean water measurements, any impact of the atmosphere cancels out.
We changed the text to make it clearer and also clarified the important aspect mentioned by the referee.

5040.26: I do not understand why measurements with 100 ms integration time have no "temporal evolution". Perhaps you should better state that the scene did not change significantly during such a short measurement time.
Changed

5042.3: Please specify what you mean with "correction spectra" (it becomes clear much later).

Text changed and specified.

Section 4.1 is very technical and also a bit difficult to understand. Why do you need to interpolate the literature spectrum exactly on a 0.1 nm grid, and not on the grid of your detector? Why should "sharp peaks" occur if you interpolate linearly (or do you mean a lack of smoothness)? A spline interpolation of spectral data is a very common procedure that does not need to be discussed in detail. Furthermore, you state later on (sect. 4.4) that the differences between linearly interpolated and spline interpolatedspectrum are negligible. Therefore I suggest to remove section 4.1 and replace it witha short statement that describes how the spectrum has been treated.
We agree that this is a bit technical and reveals nothing new. We replaced it by a short statement following the suggestion of the referee.

Section 4.2: It is stated that spectral structures of VRS and H2Oliq are closely linked to each other, which means that both can be summarized to a single correction spectrum instead of fitting these structures independently. Empirical evidence from the PCA analysis of the residual data is presented (which I assume is valid), but I do not agree with the explanation of this feature: Why should the strength of VRS structures (proportional to the amount of Raman scattered light relative to the total intensity) be proportional to the length of the light path?
In principle, the answer was already given to the referee's comment to line 5030.7 above. The liquid water absorption is proportional to the number of water molecules integrated along the absorption path which in the case of constant density is proportional to the light path: $SC_{liq} = c*L$. Please note that Referee 2 has pointed out the important issue that the assumption here is pure water and no chlorophyll absorption which would have a vertical profile.
The VRS filling-in is proportional to the number of Raman-scattered photons I_{ram} relative to the total number of photons I_{tot} (see 5030.7). I_{ram} is proportional to I_{tot} and the number of scatterers, i.e. the number of water molecules along the light path. Taking this in a formula:
$SC_{ram} = d*I_{ram}/I_{tot} = d*e*(I_{tot}*L)/I_{tot} = f*L$

Section 4.3: You mention that your approach leads to a correction spectrum that represents only the broad-banded VRS structures. However, the correction spectra shown in Fig. 5a show significant narrow-banded structures which are similar to the VRS structures shown in fig. 4 (see also comment 5054.2 below). Can you comment on this?
We agree that some incompletely removed Fraunhofer lines can be seen in the H_2O_{res} spectrum meaning that the compensation of narrow-banded lines by the intensity offset does not work perfectly. However, most of the lines are removed or strongly suppressed. To be more precise, we added the sentence "Small-band structures are suppressed to a large extent in the average residuals as a consequence of the applied straylight correction" in sect. 4.4.
We thought about applying a low pass filter but left the correction spectrum as it is because using it as a cross-section instead of VRS then accounts exactly for these leftover Fraunhofer structures that might not be well captured by the intensity offset. However, the H_2O_{res} spectrum works better than using VRS as demonstrated, which is most likely not because it captures VRS better, but because it compensates insufficiencies of the liquid water absorption.

5045.20: It would be useful to have some error discussion on the resulting H_2O_{res}spectrum, e.g. based on the standard deviation of the averaged residual spectra.

In the revised manuscript, we provide error bars in Fig. 5b from the averaging (in Fig. 5a one cannot see anything when including error bars, so we limit this to Fig. 5b). However, this provides no interesting new aspects except that the spectral structures of the H_2O_{res} spectrum are larger than the standard deviations giving further support to our statement that this is a stable residual pattern which was present in all averaged measurements. In the revised manuscript we included this in the text.

5046.3ff: Again, the differences between linearly interpolated and spline interpolated liquid water absorption spectrum represent a very technical aspect which does not deserve such a lengthy discussion, in particular since the differences between both turn out to be negligible. I also suggest to removefig. 5b which does not give any support to the findings of this paper.

We agree and replaced the technical discussion in Sect. 4.1 by a short comment (see above) and shortened technical explanations concerning this topic elsewhere. However, we find it important (and honest) to demonstrate that the H_2O_{res} spectrum is different from the changes performed to the Pope & Fry (1997) spectrum. Furthermore, we mentioned in this context that it is different from other water constituents like chlorophyll. Therefore, we kept Fig. 5b in the revised version.

5046.26: I do not really understand why the use of the H_2O_{res} spectrum instead of the VRS spectrum helps the reliability of the DOAS fit. In a DOAS fit, two very similar (linearly dependent) spectra will be subject to a very high fit error (or a failed matrix inversion), but this should not affect the results of the other absorbers.

We agree with the referee‘s opinion and removed this point.

5047.3: What do you mean with “real NO_2analysis”? Please specify.

We meant NO_2 DOAS observations in off-axis directions close to the horizon (where tropospheric NO_2 is usually analyzed). The term “real” should just make a clear break because in the sections before we were using the straight-water-pointing measurements. We changed the explanation in the text.

5047.13: It is not clear what “vertical scanning measurements” means. Do you mean MAX-DOAS measurements?

Yes, we explained in Sect. 3.5 that we were using (a) measurements pointing straight towards the water surface in order to retrieve H_2O_{res} and (b) off-axis measurements in order to retrieve tropospheric NO_2. Here we applied the H_2O_{res} spectrum retrieved in (a) on NO_2 measurements (b). We changed the text and explained this better.

5049.20: The argument that $NO_2$is found correctly if it is present in the measurements is circular. Apart from the results of the different fits, how do you know that it is really present in the atmosphere? And how do you judge which fit scenario yields correct results without consulting independent measurements? In my opinion, a reasonable argumentation would be to state that the negative NO_2SCDs from Fit1 are physically not meaningful, whereas results from Fit2 (and to a certain extent also Fit3) are always above zero, and that Fit2 is equal to Fit1 whenever NO_2SCDs from Fit1 are above zero. Thus results from Fit2 are more realistic and likely to be closer to the truth.

Yes, this is exactly what we meant. We changed the text accordingly.

5049.23 and 5050.20: It is not clear what you mean with “positive NO_2values” (I guess the NO_2SCDs from Fit3).

Yes, we changed “values” into “slant columns”.

5050.2: The statement that the amount of contamination with liquid water structures affects the NO_2error should be supported by a figure showing the NO_2fit error as a function of H_2O_{res}, or alternatively by figures similar to Fig. 7c and d, but with the H_2O_{res}fit coefficient as color code.

Sorry, this is a misunderstanding. With “error” we meant in this context the “introduced misfit of NO_2” (i.e. the degree to which the slant columns are negative). In the revised version we changed that following the referee’s suggestion.

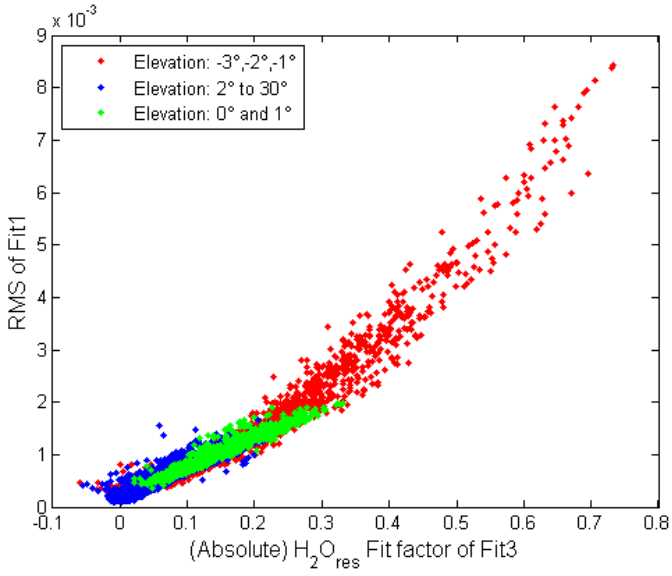

Fig. B1: H_2O_{res} SC vs RMS of Fit1

For information, we provide here a plot (Fig. B1) showing the RMS of Fit1 vs the H_2O_{res} fit factor from Fit 3. Obviously, the larger the H_2O_{res} fit factor is, the larger is the RMS in Fit1 (which is what the referee asked for) and in general the fit factor increases with decreasing elevation angle.

However, we did not add this figure to the revised manuscript, because it is pretty obvious that the liquid water effects are larger for smaller elevation angles and from Fig. 7 it is obvious that the RMS increases for decreasing elevation angles. So the figure above provides no new information.

5051.11: It is not clear for which time period the data for Table 3 has been averaged.

The averaging was performed for the whole campaign. We included this information in Tab. 3 and in the text.

5052.6: Why did you analyse OMI data for a different period than the Transbrom campaign?

We wanted to demonstrate that our findings are generally applicable and not limited to the conditions found during TransBrom, and that the retrieved spectrum is able to

improve the DOAS fit even for another instrument on another platform in a different time period (stated in the second paragraph of Sect. 6).

5052.13: The OMI data is not only shown for a different period, but more importantly also for different regions of the world.
Yes, the point to demonstrate is that it correlates on a global scale with the pattern of liquid water absorption (Fig. 1). We included "… on a global scale" in 5052.10.

5054.2: "Differential broad-band absorption" is somehow a contradiction, since the term "differential" usually refers to narrow-band structures which is the opposite of broad-band structures. I think here the difficulty is that the frequency distribution of the retrieved H_2O_{res}spectrum lies between the narrow-band structures from the VRS (which are approximately proportional to the inverse of the intensity and removed by the intensity offset) and the broad-band absorption which has been removed by the DOAS polynomial.
We agree and changed the text accordingly.

5054.15: I do not understand why you state that the improvement of satellite retrievals using the new H_2O_{res}spectrum is not the topic of your study, as you did show in Section 6 that it leads to a significant improvement.
With this section we wanted to confirm that our retrieved spectrum really accounts for liquid water effects and has the potential to improve not only MAX-DOAS fits (by reducing the RMS) but also satellite measurements over clean water surfaces. However, the focus of the study is on MAX-DOAS where the H_2O_{res} spectrum can be included when measuring over the ocean. For satellite data, a lot of additional things have to be clarified that are beyond the scope of this study, e.g. interferences of the H_2O_{res} spectrum with broad-band sand structures (briefly mentioned but not shown here), interferences with other correction spectra (for example ETA in GOME-2 data). This is too comprehensive for the present study.

Technical corrections

It would be much more convenient for the reader if most figures would have legends instead of descriptions of the meaning of the different lines in the figure captions.
This is a question of personal preferences, e.g. Referee 2 asked for removing the legend from Fig. 7. In the revised version, we provide legends for plots with more than 2 color-codings, i.e. Fig. 5, Fig. 6 and Fig. 7. In addition, we put the description always in the figure caption.
In this context, please note that we corrected the legend of Fig. 7 where the description of blue and green data points was mixed up (in the text it was correct).

5028.7: "…not considered or compensated for…"
Changed

5028.10: Replace "MAX-DOAS measurements were performed into very clear naturalWaters…" with something like "MAX-DOAS measurements of light penetrating very clear natural waters were performed…".
Changed

5028.18: The sentence “This was not achieved using a liquid water cross section…” is ambiguous since it could also imply that you did not make the attempt to use a liquid water cross section.
Changed

5029.2: Replace “Visible” with “visible wavelength range” (here and anywhere else).
Changed

5029.14: “…both absorption and in-filling of Fraunhofer lines by liquid water…”
Changed

5029.18: “For example” -> “As an example”
Changed

5031.13: “…requires a spectra resolution…”
Changed

5031.22: “…applies not to…” -> “…does not apply to…”
Changed

5031.26: “remarkable” -> “remarkably”
Changed

5033.28: “…the high density of water” -> “…its high density”
Changed

5035.7 and 5035.9: “Brillouin Scattering” -> “Brillouin scattering”
Changed

5035.8: “the water” -> “water”
Changed

5035.13: “linewidth” -> “line width”
Changed

5036.19: “k in [0, 2]
Changed

5037.18, 5041.6, 5042.4, 5051.7 5052.3, 5052.22: You use “therefore” (= “for this reason”), but you mean instead “for this purpose”
Changed

5040.20: Replace “cleanliness” with, e.g., “purity”.
Changed

5042.1: I suggest to replace “experimental spectra” with “empirical spectra” (here and anywhere else). “experimental” has the connotation of something incomplete. Why did you put the term “correction” into brackets?

Changed. We used brackets here, because in the first two subsections we did not try to retrieve a correction spectrum for an existing literature cross-section, but an entire improved cross-section from the measurements.

5043.13: “old” -> “initial”
Changed

5045.20: I guess you mean “individual fit range” when you state “DOAS fit”
Changed to “parameter set”

5047.4: “fit” -> “fit settings”
Changed

5047.24: “clear” -> “distinct”
Changed

5049.3: “(almost) no NO_2” -> “very low NO_2”. Here a quantification of a mean value or an upper limit would be useful.
Changed

5049.15: “problem” -> “problems”
Changed

5049.16: “effect” -> “effects”
Changed

5049.19: “independently” -> “independent”
Changed

5054.6: “reasonable” -> “meaningful”
Changed

Are Fig. 1 and Fig. 8 showing monthly means? Please specify
Yes, they are monthly averages of August 2007 (Table 4). We now specified this in the figure caption.