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Interactive comment on "New insights into OH airglow modelling to derive night-time atomic oxygen and atomic hydrogen in the mesopause region" *by* Tilo Fytterer et al.

Anonymous Referee #2

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General comments:

This study proposes a new OH airglow model to retrieve O and H densities in the mesosphere. The OH model is empirically developed to simultaneously fit four OH emissions observed by the SABER/TIMED instrument at 2.0- and 1.6-microns as well as the OH(6-2) and OH(3-1) bands measured by SCIAMACHY/ENVISAT. The authors show that using adjusted rate coefficients and specific state-to-state relaxation mechanisms, the OH model reproduces the four emissions. However, they retrieve very high O and H concentrations.

The concept of fitting four emission bands simultaneously is promising as it may con-

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strain unknown parameters involved in modeling OH emissions. The conclusions regarding their new OH model, however, are speculative as model inputs used in the study to simulate emissions have larger uncertainties than the authors claim (i.e. Einstein coefficients, ozone concentration). Accounting for these uncertainties will significantly alter the results of this paper. Further, the authors show that the applied OH model retrieves unrealistically high atomic oxygen and hydrogen in the MLT. Recent publications (s.f. Kaufmann et al. 2014, Mlynczak et al. 2018, Panka et al. 2018, and Zhu and Kaufmann 2018) have shown that [O] densities retrieved using SABER and SCIAMACHY measurements are much lower (by up to a factor 2 and more) than those retrieved in this study, specifically from 85-100 km.

The model development (and the rate coefficient adjustments) must have a goal to reliably retrieve atmospheric properties from the observations. The very high [O] and [H] retrieved with the help of the new model indicates that there are still major flaws (it does not matter that it fits all selected emissions, this system has a very large number of unconstrained variables). The paper needs major revisions before making physical sense and being suitable for publication.

Instead of fitting four emission bands while simultaneously retrieving [O] and [H] densities, I recommend for the revised study, to concentrate on retrieving [O] and [H] densities but only fit three emission bands (as will be discussed below, the OH(6-2) emission band is unreliable and taking into account its large uncertainty will alter the results of the current study). Further, the authors must demonstrate how the rates derived from zonal mean profiles fit real single scans in three emission bands.

Specific comments:

Line 1. The title states “New insights in OH airglow modeling. . .”. The proposed new "insights" are highly speculative and are inconsistent with existing theory and experiments. The authors need to first show that reliable [O] and [H] can be derived when their OH model is applied before claiming any new insights.

In the introduction section, discussion regarding the current progress of [O] and [H] retrievals using SABER and SCIAMACHY instruments is missing. Retrieving these two parameters are a key point of this study and no background is given. Please cite recent [O] and [H] retrieval studies and their proper discussion.

Lines 175-185. The retrieval of [O] and [H] are both dependent on the [O_3] volume mixing ratio. The authors used nighttime [O_3] taken from SABER. The nighttime SABER [O_3] has never been rigorously validated, nor is there a paper discussing its retrieval approach. Differences between WACCM and SABER [O_3] are roughly a factor of 2 (Smith et al. 2014) and, therefore, one cannot rely on SABER [O_3] as an input parameter. Additionally, in Mlynczak et al. 2018, the conclusion is made that current SABER daytime [O_3] and, supposedly, the nighttime one is too high based on a significantly lower [O] retrieved in that study. It is clear from equation 4a and 4b that any variation in [O_3] will have a significant effect on [O] and [H]. For the revised study, I recommend using inputs taken from a self-consistent photochemical model like WACCM instead of ones taken from retrievals, which are not supported by any other studies. Additionally, uncertainties in the retrieved parameters due to large uncertainties in the [O_3] must be estimated and discussed.

Lines 268-269. "...we exclude the Einstein coefficients as a potential fundamental error source." I do not agree with this statement. The new constraint imposed using the OH(6-2) emission band is unreliable. This band has a very small Einstein coefficient. The authors do not go into detail regarding the numerical differences among the literature of the OH(6-2) emission rate, but state that they are consistent. The authors use the OH(6-2) coefficient taken from Xu et al. 2012 which is 1.767 sec^{-1}. A more recent publication by Brooke et al. (2015) recalculated OH Einstein coefficients and found a rate of 1.16 sec^{-1} for the same transition. The rate of Xu et al. (2012) is approximately 50% larger than that of Brooke et al. (2015) and would significantly change the OH(6-2) emission profiles in Figures 1-4 as well as the results in Tables 2 and 3. The ab initio calculations of van der Loo and Groenenboom (2007, 2008) give values that are even smaller than Brooke et al. (2015) - the OH(6-2) emission rate of Xu et al. (2012) is 75% larger than that of van der Loo and Groenenboom (2007, 2008). Evidently, the issue of the OH Einstein coefficients is not yet settled. To make matters worse, the SCIAMACHY OH(6-2) band displays a signal count two orders of magnitude smaller than that of the OH(3-1) band. The uncertainty of the VER signals for these two bands will be vastly different. Finally, because these two bands have a different Delta v and values of Einstein coefficients that are different by more than one order of magnitude, the uncertainty of the OH(6-2) band will be much larger. Therefore, both the observed low VER signals and the large uncertainty in the value of the Einstein coefficient indicate knowledge of the OH(6-2) band is highly uncertain. As a result, the OH(6-2) emission band cannot be confidently used to constrain OH modeling parameters. For manuscript revisions, I recommend to redo this study using only three OH emission bands. An alternative would be to validate the intensity of the OH(6-2) band by comparison with the OH(6-3) profile, which should be within the capabilities of SCIAMACHY.

Lines 493-498. “Applying their suggested limit, we found that in our case chemical equilibrium of O3 is probably true only above 80 km.” Recent studies have shown that the [O] and [H] retrieval approach used in this study may be flawed (Belikovich et al., 2018; Kulikov et al., 2017, 2018) and can introduce additional uncertainties. The authors addressed these issues very briefly here, but this needed to be more rigorously discussed. To say just simply “probably true” is insufficient. Additionally, uncertainties of the final results related to a probable chemical equilibrium breakdown need to be estimated and discussed.

Lines 521-522. “. . .we think that the O(^{3}P) and H derived by the Best-fit model provides reasonable results between 80 and 95 km.” The [O] derived looks somewhat reasonable only below 87 km, but not above this altitude. At 95 km, the retrieved [O] is at least two times larger than Mlynczak et al. [2018] and more than a factor of 5 at 100 km. It has also been discussed in detail that high [O] will disrupt the energy balance in the MLT (Mlynczak et al. 2013, 2018) and influence temperature retrievals. If, in the revised study, the retrieved [O] and [H] remain high, then please demonstrate how it impacts the heating and cooling of MLT and discuss in detail possible ways to overcome the corresponding energy budget imbalance.

Line 537-539. "Furthermore, it cannot distinguish between OH(5) and OH(4) as a well as OH(9) and OH(8), and consequentially errors in OH(5) and OH(9) might be compensated by errors in OH(4) and OH(8) or vice versa". This is a troubling statement as your main results in Table 3 (R11a, R11b, R11c, R11d, and R11g) involve these levels and describe rate coefficients for specific state-to-state reactions. This statement needs to be clarified. It sounds as if you treat OH(9)+OH(8) as a combined, single level as well as OH(5)+OH(4). Is this true? If you cannot distinguish between certain vibrational levels, then how can you determine rate coefficients for specific vibrational levels?

Tables 2 3. It is not clear if the results in Table 2 and 3 describe the Best-Fit model discussed in the conclusion. Table 2 shows empirically determined branching ratios of the OH(v) + O_2 reaction for only VER observations "below 85 km" while Table 3 shows the branching ratios of the OH(v) + O(^{3}P) reaction for only VER observations "above 85 km". The lack of consistency adds confusion to the findings of this study. Please clarify this. Is there not a best-fit model for altitudes 80-100 km?

Table 3. The two most important processes (largest rate coefficients) estimated from the best fits are not energetically allowed! Processes R11a and R11c are highly endothermic processes by ~3000 cm^{-1} and 2000 cm^{-1}, respectively. Additionally, the state-to-state rate coefficients in Table 3 for the OH+O(^{3}P) reaction appear to be in contradiction with the findings of Kalogerakis et al. (2016), who measured a large rate coefficient attributed to the resonant reaction OH(9)+O(^{3}P) $\rightarrow$ OH(3)+O(^{1}D). These results are non-physical and must be revised. As stated above, it seems most likely that fitting the highly uncertain OH(6-2) signal that has large systematic errors have skewed the results of this paper. Removing this constraint may bring the revised OH

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model into better agreement with recent laboratory and modeling studies as well as retrieve reasonable [O] and [H].

Figures 1-4. Why are there no error bars displayed for the measured OH(5-3)+OH(4-2) VER emissions despite error bars displayed for the OH(6-2) and OH(3-1) emissions? In general, the concept of fitting the zonal mean profiles for three OH bands is questionable. Operating with zonal mean profiles only, the authors are essentially fitting a single scenario (four individual signal scans). They must demonstrate how the rates derived from zonal mean profiles fit real single scans in measured emission bands. This will show whether the derived rates have any value for practical analysis of measurements of both instruments.

Technical corrections:

Line 26-28. This sentence needs a citation at the end.

Lines 535-539. These sentences should be moved to section 2.3: The OH airglow Base model.

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