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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Implications of the O + OH reaction in hydroxyl nightglow modeling" *by* P. J. S. B. Caridade et al.

Anonymous Referee #2

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This manuscript should not be published in its current form and requires major revision prior to publication. There are two significant issues. The first concerns having the most up to date OH modeling and experimental references in the manuscript and the second concerns how the results from the Adler-Golden reference are used in the modeling study.

This manuscript is missing two key references that were published in 2011 and 2012. The first reference is Xu et al. Source: JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES Volume: 117 Article Number: D02301 DOI: 10.1029/2011JD016342 Published: JAN 19 2012. This manuscript describes an OH emission modeling study similar in scope to the work described here and the authors of this work need to compare and contrast to the results of Xu et al. The Xu et al. work does a good job

of reviewing modern modeling and observations and the more recent references in that manuscript should be incorporated also. The second is a laboratory measurement of the collisional removal rate constant for OH(v = 9) by oxygen atoms that disagrees with the results of the calculations recalculated in this work. A value approximately seven times larger is obtained at room temperature. This inconsistency needs to be addressed and discussed. The reference is Kalogerakis et al. Journal of Geophysical Research-Atmospheres Volume: 116 Article Number: D20307 DOI:10.1029/2011JD015734 Published Oct 20 2011. Based on these omissions, I anticipate significant revisions will be required.

The second major issue concerns the use of the results from the Adler-Golden reference. One of the key points examined in this work is the OH + O rate constants used by Adler-Golden. Adler-Golden made the assumption on the rate and pathways of the OH + O described in this work but they then used that assumption to extract the degree of multiquantum relaxation for the main oxygen molecule collider via comparison to OH observations. In the variables of Adler-Golden they obtained the C parameter via a fit to the observable. The Caridade et al. manuscript uses the Adler-Golden fit oxygen molecule state to state rate constants without realizing that those fit rate constants already have the OH + O rate constant assumption incorporated in them. Putting a new set of rate constants in for OH + O invalidates the fit done by Adler-Golden and there extracted oxygen molecule state to state rate constants would need to be modified. Based on this problem the modeling and conclusions need to be reexamined.

Here is a list of minor points that should be addressed in a revised manuscript.

1) First sentence of abstract. The term "more realistic estimates" could simply be replaced by calculated.

2) Line 6 of abstract. The term significant is used. It would be good to be somewhat quantitative

3) The first sentence of the paper is a gross overstatement of the status of our lack of

understanding of the terrestrial atmosphere.

4) Page 6487 line 6. This is an overstatement; I think most models where non-LTE issues are important incorporate them.

5) Page 6488 line 4 replace LL with LI

6) Page 6488 line 26 should add “and atmospheric observations.” after measurements.

7) Page 6488 line 27. I think this should state rocket observations not satellite observations

8) The first sentence of Section 2 overstates the importance of O + OH in my opinion. The term masterpiece seems over the top.

9) Page 6490 line 8. The term re-analyzed is used but there is not description of how or why it was reanalyzed.

10) Page 6490 line 21 The text mentions method I but I do not think it is described elsewhere.

11) Page 6490 line 25 The private communication should also reference the publication that resulted from that work Cosby et al. Source: CANADIAN JOURNAL OF PHYSICS Volume: 85 Issue: 2 Pages: 77-99 DOI: 10.1139/P06-088 Published: FEB 2007

12) Page 6492 line 18. This sentence seems to confuse measurement of the v = 0 reaction rate with the v = 1 total removal rate constant. I cannot locate what the calculated rate for v = 0 reaction is using this approach and how does it compare to experimental values.

13) Page 6497 line 10. How do the calculations made for OH + O2 compare to the many laboratory based measurements of that process?

14) Page 6501 Line 17 Describe the viewing geometry used to calculate the profiles in Fig. 6.

15) Page 6501 starting line 27. The steady state paragraph is extremely unclear and provides little value to the entire manuscript. I do not understand how if you start with the steady state concentrations that you get any change in the concentrations (page 6502 lines 11 and 12). It is clear from Fig. 7 that was not the starting point. For a more complete of steady state issues look at the Xu et al reference given above. I think the entire steady state section should be removed.

16) Page 6502 line 18. The term accurate is used as the first word of the conclusion but I cannot find in the manuscript as discussion of the accuracy of the calculated rate constants.

17) Table 1. The units on the rate constant appear incorrect. Also I think using three significant figures in the table for the calculated rate constant overstates the accuracy of the calculations.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 6485, 2012.