

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

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*Referee:* This manuscript should not be published in its current form and requires major revision prior to publication.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.

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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.

*Reply:* Thank you. We were not aware of such a work when the manuscript was completed: the Journals were not easy to access and we had no hint of them through cross-referencing, specially the one by Xu et al. The following paragraphs have been added to the text.

In page 5, line 3: “Such a value seems to be corroborated (Pickett et al., 2006) by upper atmospheric measurements, although it has also been questioned (von Clarmann et al., 2010) due to predicting a smaller population of hydroxyl radicals than observed. Quoting the authors (von Clarmann et al., 2010), “it may provide an upper limit for the reaction”. Indeed, the topic has long been a matter of uncertainty. Persisting doubts have most recently been expressed (Xu et al., 2012) as “The question of whether the reaction with or quenching by atomic oxygen depends on the OH vibrational level could not be resolved; assumptions of vibrational level dependence and independence both gave good fits to the observed emissions.” This follows previous argumentation (Smith et al., 2010) where the question of the vibrational dependence of the rate of removal of OH( $v$ ) by atomic oxygen has been raised when developing the SABER (Sounding of the Atmosphere using Broad-band Emission Radiometry) algorithm. The authors have in this case utilized a value of  $5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  for the reaction with OH( $v = 9$ ) and OH( $v = 8$ ), which is about twice

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the rate for reaction of the ground state of OH with atomic oxygen at mesospheric temperatures (Spencer and Glass, 1977) and essentially coincidental with the calculated value (Varandas, 2004a) for  $\text{OH}(v = 9)$ . Moreover, it has been noted (Mlynczak, 2008) that testing of a larger rate constant of ( $\sim 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ), reported by (Copeland et al., 2006) from laboratory measurements but still about half of another experimental value most recently reported (Kalogerakis et al., 2011), was found to give unphysically large values of atomic oxygen, energy deposition, and heating rates."

In page 9, after line 3: "As noted in the Introduction, Kalogerakis et al. (2011) have recently reported a collisional removal of  $\text{OH}(v = 9)$  by several quenchers using laser fluorescence spectroscopy to measure the steady-state population. The rate constant reported was  $4 \pm 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for the  $\text{O} + \text{OH}(v = 9)$  relaxation, a value nearly 7 times larger than the one here utilized. Although a reason for the smaller theoretical value may be ascribed to unknown subtleties of the  $\text{HO}_2$  PES or even nonadiabatic effects that could not have been taken into account, there are pending issues that obscure any definite conclusion at present. In particular, as also noted above, the use of very large rate constants lead to unrealistic values of  $[\text{H}]$ ,  $[\text{O}]$  and for the mesospheric chemical heating rate (Mlynczak, 2008). Although stated (Kalogerakis et al., 2011) that the tendency for smaller rate constant values is due to the uncertainty of some parameters used in the kinetic models, and the SABER data will yield more accurate results when using high rate constant values, such a trend has not observed in the work of Xu et al. (2012) who suggested "a value of  $6.465 \pm 0.785 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ", about 20% larger than the calculated value for  $\text{OH}(v = 9)$ ."

*Referee:* 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  $\text{OH} + \text{O}$  rate constants used by Adler-Golden. Adler-Golden made the assumption on the rate and

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pathways of the  $\text{OH} + \text{O}$  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  $\text{OH} + \text{O}$  rate constant assumption incorporated in them. Putting a new set of rate constants in for  $\text{OH} + \text{O}$  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.

*Reply:* We agree with the point raised but an answer to this issue is beyond the scope of the present work. So, the assumption has been made that the values extracted by Adler-Golden for the other reactions are still realistic. Whether this is truly the case remains to be seen either empirically by redoing Adler-Golden's work or through the use of accurate experimental/theoretical state-to-state results (which to our knowledge are unavailable). This will be emphasized on the text.

In page 12, end of line 11: "It should be pointed at this stage that Adler-Golden used the assumption above on the rate of the  $\text{O} + \text{OH}(v)$  to extract the degree of multiquantum relaxation for the main oxygen molecule collider via comparison to OH observations. For consistency, we should therefore re-evaluate the latter data using our own set of  $\text{O} + \text{OH}(v)$  rate constants, as pointed out by an anonymous Referee to whom we wish to thank. Clearly, this task lies out of the scope of the present work. The assumption is therefore made that the values extracted by Adler-Golden for the other reactions are still realistic. Whether this is truly the case remains to be seen either empirically by redoing Adler-Golden's work or through the use of accurate experimental/theoretical state-to-state results, which to our knowledge are unavailable."

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*Referee:* 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.

*Reply:* Done, thanks.

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

*Reply:* The text now reads: “Significant differences in the vertical profiles of vibrationally excited hydroxyl radicals are obtained relative to the ones predicted by Adler-Golden (1997) when employing an  $\text{OH}(v') + \text{O}$  effective rate constant fixed at twice the experimental value for quenching of  $\text{OH}(v' = 1)$ . At an altitude of 90 km, such deviations range from  $\sim 80\%$  for  $v' = 1$  to only a few percent for  $v' = 9$ .”

*Referee:* 3) The first sentence of the paper is a gross overstatement of the status of our lack of understanding of the terrestrial atmosphere.

*Reply:* It has been rephrased as: “Well known mysteries in terrestrial atmosphere (Crutzen, 1997), many still unsolved, have stimulated the study of reactions and chemical cycles (Slanger et al., 1988; Toumi et al., 1996; Varandas 2002, 2005a) focusing on regions of the middle atmosphere (stratosphere and mesosphere)”.

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

*Reply:* Indeed, but for the physics part. We have rephrased the text as follows: “Although several studies have been devoted to the role of vibrationally excited species in reactions, particularly for the  $\text{HO}_x$  cycle, atmospheric chemistry models of the stratosphere and upper layers often neglect non-LTE (see, e.g., von Clarmann et al. (2010) and references therein). Indeed, as noted elsewhere (von Clarmann et al., 2010) it has become a standard procedure to consider non-LTE radiative processes associated with vibrational and rotational excitation in radiative transfer modeling and remote sensing data analysis whenever appropriate (e.g., Funke et al., 2001a,b; Kaufmann et al., 2003; Yankovsky and Manuilova, 2006), but consideration of these effects in chemistry modelling is by far no standard today (von Clarmann et al., 2010).”

*Referee:* 5) Page 6488 line 4 replace LL with LI.

*Reply:* Done.

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

*Reply:* Done.

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

*Reply:* Thank you, done.

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

*Reply:* Modified, it now reads: "The O + OH reaction has been widely studied experimentally as it is of key importance in many interdisciplinary areas (Miller et al., 1990; Smith et al., 2004; Varandas, 2007; Smith et al., 2010; Kalogerakis et al., 2011)."

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

*Reply:* The term "re-analyzed" has been applied only to imply that part of the results now presented have not been published in the original Chemical Physics Letters papers (2004a,2007). The results have in no way been revised or modified, with novel convergence checks now done corroborating the published ones. See pg 6489, lines 15-18 and page 6491, line 3.

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

*Reply:* The text now reads: "The calculations by method I (where the impact parameter for running the trajectories has been fixed equal for all initial vibrational states) reported elsewhere (Varandas, 2004a) use for each temperature a steady-state distribution that mimics the vibrational states of OH in the upper atmosphere (Varandas, 2003)."

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*Referee:* 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

*Reply:* We have included the reference which was unknown to us, thank you.

*Referee:* 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.

*Reply:* We have now added: "Khachatrian and Dagdigian (2005) reported a total removal rate constant for OH( $v = 1$ ) at room-temperature of  $3.9 \pm 0.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , with the recommended values of IUPAC (Atkinson et al., 2004) and NASA (Sander et al., 2006) being  $3.5 \pm 0.1$  and  $3.3 \pm 0.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , respectively. Note that the rate constant for OH( $v = 0$ ) is  $\sim 2.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (Varandas, 2004a).

*Referee:* 13) Page 6497 line 10. How do the calculations made for OH + O<sub>2</sub> compare to the many laboratory based measurements of that process?

*Reply:* The calculations (Caridade et al. 2002) have yielded a value about 4 times larger than the experimental ones, which may partly reflect difficulties in getting an accurate pes for HO<sub>3</sub> [Yu and Varandas, Chem. Phys. Lett., 334, 173 (2001)]. Since we are interested in assessing the importance of the O + OH reaction, such

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values would not add anything reliable to the discussion, and hence have not been considered.

*Referee:* 14) Page 6501 Line 17 Describe the viewing geometry used to calculate the profiles in

*Reply:* Caption of Fig. 6 now reads: "Vertical profiles of the volume emission rate for the 8-3 band obtained using the empirical  $O + OH(v')$  rate constant from Adler-Golden (1997) and those from the present work based on the QCT calculations from Varandas (2004a). Also shown are the original reported data of Adler-Golden (1997) and the ETON5 experimental zenith intensity measurements (McDade et al., 1987)."

*Referee:* 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.

*Reply:* We could remove the paragraph and simply note that the steady-state approximation had been tested. However, we still believe that the material deserves being reported since the SS assumption is seldom evaluated (even in recent papers). Moreover, the other anonymous Reviewer did not ask for deleting such a material. So, we hope to maintain it as is except for the minor correction required to answer reviewer #1: There was a misprint, it should read: "In all cases, the nascent concentrations were taken as the starting point."

*Referee:* 16) Page 6502 line 18. The term accurate is used as the first word of

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the conclusion but I cannot find in the manuscript as discussion of the accuracy of the calculated rate constants.

*Reply:* Although the accuracy has been clearly reported by Varandas (2004), we see nothing wrong in being less demanding and replacing the word "accurate" by "reliable" as now done.

*Referee:* 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.

*Reply:* Thank you for pointing this misprint. Regarding the significant figures, the error is expected to be of 5-10% or so if only due to the  $O+OH$  rate constants. Since a precise estimation of error is essentially impossible, we keep the same number of figures as before but note that it is only done for convenience.

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