

***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: On the whole the work is well placed into the context of existing work, with a lot of references. However, some more recent articles may also be relevant in this context, e.g. Xu et al., J. Geophys. Res. 117, D02301, 22 pp., 2012 doi:10.1029/2011JD016342, and possibly references therein.

Reply: Fully agreed, such papers appeared after the work has been completed. We have included both the reference and relevant comments along the text.

Referee: p 6486 line 9: This statement is a bit vague. Please specify the “Other
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limiting cases”. If this refers to the “sudden death” and “collisional cascade” limiting cases: These technical terms are well enough known that they can (to my judgement) be used in the abstract without definition.

Reply: We have altered the abstract as suggested. It now reads: “Other limiting cases reported in the literature, namely the sudden-death and collisional cascade, are also discussed.”

Referee: p 6484 line 16: I suggest to delete “that are critical for the sustainability of life on Earth”. While this certainly is true, this sounds a bit lurid and does not really help the paper. I guess that more than 99.9 percent of ACP articles treat atmospheric regions which are in some way critical for the sustainability of life on Earth.

Reply: Agreed.

Referee: p 6486 line 22: Is the Earth’s “upper atmosphere” meant here (“...low pressures found in the upper atmosphere”)? I first understood it this way, but the next sentence makes a statement on the first application to the terrestrial atmosphere, suggesting that in line 22 still something else is meant, and I was left confused. I guess that indeed the Earth’s atmosphere is meant (because otherwise the restriction to the upper atmosphere would make no sense, e.g. on Mars the pressure is already low near to the surface). To make a long story short, I suggest to modify line 22 to “...found in the Earth’s upper atmosphere”.

Reply: Suggestion accepted, thank you.

Referee: p 6487 line 1: "physical chemistry properties" sounds a bit funny to me. While pressure and temperature certainly have influence on the chemistry, these are physical properties.

Reply: It now reads "Due to the low pressures and temperatures at high atmospheric altitudes, vibrationally excited molecules may have significant lifetimes."

Referee: p 6487 lines 7/8: In this context the statement is a bit too general. It should be restricted to atmospheric chemistry models (chemistry-transport models and chemistry-climate models. Other models, like radiative transfer models, often include non-LTE.

Reply: It now reads "atmospheric chemistry models".

Referee: p 6487 line 12/13: I do not quite understand this: If we had accurate knowledge on the excitation and de-excitation rate coefficients, couldn't we accurately model the required vertical profiles? Is this really "another reason" or is this just another view on the same reason? Or does the statement refer to other species? Please clarify.

Reply: The sentence appears correct and indeed addresses any relevant species. It now reads: "One of the reasons pointed out (McDade et al., 1987; Adler-Golden, 1997) is the lack of accurate state-to-state deactivation and state-specific rate constants for key reactions involved in the atmospheric cycles. Another is due to the non-existence of accurate vertical profiles for the different vibrationally excited species."

Referee: p 6488 line 5: "that any ... does not". The grammar of this sounds a

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bit funny to me and I would say "that no relaxation process contributes...". However, since I am not a native English speaker, all my language recommendations should be used with care.

Reply: Suggestion accepted.

Referee: p 6488 line 14: I am not familiar with the term "rationalization" in this context (and elsewhere in this paper). If this is a technical term I am just not familiar with, then it is ok; otherwise, I have seen the term "fractionation" to describe which fraction is in which state.

Reply: We have kept as is, since we see nothing wrong with it. However, part of the misunderstanding may have arisen due to the writing which has been modified to read: "Rationalization of the nightglow spectrum depends strongly on the kinetics data and vertical profiles of OH(v), being highly relevant for atmospheric remote sensing (Pickett and Peterson, 1996)."

Referee: p 6489 line 4-7: I do not find that the use of the AG data is criticized by von Clarmann et al. They just discuss what would happen if the AG data would be used. They draw no conclusion which data set is superior.

Reply: It may be so, although we have gathered such an impression. We have now rewritten and augmented the text as follows: "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

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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 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 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."

Referee: p 6489 line 23: Not sure if "masterpiece" is the correct term here. "key issue"?

Reply: 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: p 6491 line 19: I suggest to remove the comma after QCT.

Reply: Done.

Referee: p 6492 line 9: adverb: roughly T-independent.

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Reply: Done.

Referee: p 6492 lines 12 and 14: As said above, I have some problems with the term "rationalize".

Reply: It now reads: "In all cases, the dominant contribution for large v' is the reactive contribution. This can be understood from the role played by the highly stretched OH molecule, which favours bond-breaking. Moreover, the large reactive rate constant at low temperatures can be rationalized by the prevailing long-range forces as described by capture-type dynamics (Clary and Werner, 1984; Varandas, 1987)".

Referee: p 6492 line 27: reword: theoretical data of this work.

Reply: "Clearly, his value overestimates by far both the experimental/recommended and the theoretical data from this work."

Referee: p 6494 line 6: Not sure if the expression HO _{$y+3$} is widely known, and the reader might not wish to consult the related reference. Could you state in a few words what HO _{$y+3$} is about?

Reply: "Furthermore, from the so-called HO _{$y+3$} mechanisms (Varandas, 2002) (where $y = 0, 1, 2$ labels the number of O atoms in the hydrogen-oxygen species (Varandas, 2003), say $y = 0$ for HO₃), one may have to pay attention to the reaction OH(v') + O₂(v'') as a potential sink of vibrationally excited OH.

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Referee: p 6494 Eq 3: It took a while until I figured out that the subscript CHV are the initials of the authors of the discussion paper, and that it is used to distinguish the assumption made for Eq. (3) from the other assumptions. I suggest to make clear in the text that the subscript refers to the assumptions made. It becomes more obvious in the context of Eqs 4 ff but clarification already in the context of Eq 3 would be helpful.

Reply: It escaped to our attention: label has been removed.

Referee: p 6502 line 1 "rationalization" see above.

Reply: The paragraph now reads: "A critical assumption in this work is the steady-state hypothesis, a condition frequently employed and quite often taken as granted since its proposition in the seminal work of Bodenstein (1913), Chapman and Hunderhill (1913) and Chapman (1930), with Chapman utilizing it for explaining of the ozone layer in the Earth's atmosphere."

Referee: p 6502 around l 13: I have a problem to understand the message of these lines: I assume that these tests have been made to demonstrate that the assumed steady-state concentrations are reasonable. Thus, they are fed into a time-dependent model. I do not quite understand why the steady-state assumption is considered justified if the concentrations change their values at all. If steady state is valid, I would expect that integration of the reactions over time would not change anything. I would expect flat lines. Or is this, because you initialize with $[\text{OH}(v')]_{\text{CHV}}$ but integrate for $[\text{OH}(v')]_{\text{cc}}$, which results in another set of steady-state concentrations? Perhaps the use of the term "steady state" in this manuscript is ambiguous: Sometimes it is used to specify the $[\text{OH}(v')]_{\text{CHV}}$ distribution (probably p6502, line 11), and elsewhere it is used in a more generic sense, whenever steady-state theory is used. Perhaps it is

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this ambiguous use of the term which confuses me. Or have I misunderstood anything?

Reply: There was a misprint, it should read: "In all cases, the nascent concentrations were taken as the starting point."

Referee: p 6512 fig 2: Please use larger legends; also the legends of the other figures may be a bit too small when the figures are shrunk to one-column ACP format. Or make sure that the other figures are reproduced as 2-column figures.

Reply: Font size of labels has been changed for all plots. Figures 2 and 4 will be suggested as 2-column ones.

Referee: p 6517 fig 7: The axis caption 104 t/s is certainly correct but this way to report the magnitude is not very common. Could you use milliseconds or microseconds for the time axis?

Reply: We have now changed to milliseconds.

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

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