Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-766-RC2, 2016

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Resolving the mesospheric nighttime 4.3 µm emission puzzle: New model calculations improve agreement with SABER observations" *by* Peter A. Panka et al.

Anonymous Referee #3

Received and published: 20 December 2016

General comment.

The manuscript proposes an alternative mechanism to that of Lopez-Puertas et al. (2004) (LP04) for explaining the N2(v=1) excitation that gives rise to an enhanced CO2 4.3 μm night-time emission as measured by SABER. Such mechanism is compatible with that proposed by those authors but the energy is transferred through an intermediate pathway. It then represents an important research finding that deserves to be published.

I do not fully agree however in the way it is presented at some passages. It gives the impression that the presented mechanism is the "correct" one and the previously proposed mechanism is not correct. So far only some theoretical estimates have been

carried out suggesting that the multi-quantum energy transfer from OH(v) to N2(1) is not likely, but no laboratory measurements have corroborated it. I would then be not so categorical about the new mechanism with sentences such as "... the missing night-time mechanism of CO2(v3) pumping has finally been identified."

I think the paper should be presented as being able to explain the SABER radiances with a plausible mechanism for indirect transfer of the energy from OH(v) to N2(1) instead of the direct multi-quantum energy transfer with a required efficiency of 2.8-3 as suggested by LP04.

The authors should also be cautious with assertions such as the new mechanism "improves agreement with SABER observations (in the title, as well as in the conclusions)". Both mechanisms seem to be able to explain SABER radiances with a very similar degree of agreement (Fig. 2 of the manuscript and Fig. 12 of LP04). It seems the new pathway is more plausible according to some theoretical estimates but I have not seen in the manuscript a clear discussion about why the multi-quantum mechanism should be ruled out.

Furthermore, it should be proved more quantitatively that the new proposed mechanism, that affect to the OH(v) populations, is able to explain the SABER OH measurements and that it is consistent with the multiple previous rocket measurements of OH(v).

I think these points should be addressed before the manuscript is accepted for publication.

Specific comments.

1) I think the title should be revised. The new model calculations are equally good as previous ones in reproducing SABER 4.3 μm observations. The focus should be put on the new OH(v) => N2(1) transfer mechanism rather than on the reproduction of the radiances. The agreement of the new calculations with SABER (-20,30%) are

not better that the results shown by LP04 in their Fig. 12, that in spite of the larger uncertainties in the "theoretical" reaction rates for OH(v) to O(1D) energy transfer as well as in the O abundance.

Also, I do not find appropriate the other part of the title: "Resolving the mesospheric night-time 4.3 μm emission puzzle". Where is the puzzle? LP04 already explained SABER radiances to within +/-20%. I would be more in favour of a title like "A new alternative mechanism for explaining the mesospheric night-time 4.3 μm emission" or even been being more precise, for explaining the mesospheric night-time excitation of N2(1)".

Abstract. Although the transfer of energy mentioned in the manuscript of OH(v)=> N2(v)=>CO2(v3)=4.3 μm emission, is correct it could be simplified to OH(v)=> N2(v), since the mechanism proposed affects only to this part of the transference and the remaining transfers, =>CO3(v3) => 4.3 μm, are common with the previous study.

Lines 6-8. "A previous study suggested the "direct" transfer OH(v) => N2(v) => CO2(v3) => 4.3 μm of vibrational excitation from OH(v) to CO2 in the night-time mesosphere. However, accounting for this excitation mechanism alone leads to significant underprediction (by up to 80%) of observed 4.3 μm limb radiances." See comment above. If the same mechanism is assumed as multi-quantum (with an efficiency of 2.8-3) LP04 were able to explain the SABER radiances. Hence, that sentence should be re-written. That mechanism with single quantum was not the final conclusion of LP04. Somehow the manuscript is inconsistent as this assertion is correctly mentioned in other parts or the text but not everywhere, as in theses sentences, and other important instances, as in Fig. 2.

Lines 13-14. "This finding creates new opportunities for the application of CO2 4.3 μm observations in the study of the energetics and dynamics of the night-time MLT." I am not really convinced about that. Even if the energy pathway from OH(v) to N2(1) was not clear, the previous mechanism was already able to explain the measured SABER

4.3 μm night-time radiances as well as with the new alternative mechanism.

Page 2. Par. from lines 3 to 13. I would not argue as a motivation for this research its potential use for retrieving CO2 from night-time 4.3 μm SABER measurements. I think the new mechanism is already important on its own, i.e., it is important to understand the non-LTE processes occurring in the middle atmosphere, and it does not need the motivation of CO2 night-time retrieval because this presents additional problems, which, in my view, are more important. First, I think to measure CO2 at night-time is not very important as far as we have daytime measurements for the wanted latitudes/seasons. Because, as it is very well mentioned in the manuscript, CO2 has a very long chemical lifetime, we do not expect significant (photochemical) diurnal variations. Only tides, but they would also be present in night-time observations. The only region of interest would be the polar winter, where no daytime measurements are available yet. But the retrieval of CO2 there has other problems. As it is in high latitudes, auroral excitation of N2(1) is very important and that is not well known. Also the geomagnetic conditions are very variable and hence difficult to model. In addition, as has been demonstrated by Winick et al. (1988), the location of the aurora along the LOS has to be known very well. Furthermore, most of the night-time 4.3 μm radiance comes from the strong CO2(v3) fundamental band, which is very optically thick. And last, the night-time 4.3μm signal is usually much more noisy ($\sim$a factor for 100 or larger) than the daytime one.

Page 2. Line 26 and ff. "However, using laboratory rate coefficients of corresponding reactions the authors were unable to reproduce the 4.3 μm radiance observed by SABER." This is only partially correct, as they were able to reproduce SABER radiances when using an efficiency of 2.8-3 with the same reaction rate.

Reaction R2 has been normally used as OH(v,<=10) + N2(0) <=> OH(v-1) + N2 note that N2 is not excited, see, e.g. Adler-Golden et al (1997), because it has been used in OH(v) modelling and the interest was the deactivation of OH(v), without paying any attention to the final state of N2, e.g., if it was excited or not excited. Hence, I think the statement (line 30) that "its has been accepted with a value of 1" needs more discussion. It has been used most of the times regardless of the excitation of N2. Theoretical estimates by Adler-Golden et al. (1997) and Sharma et al. (2015) suggest that it takes place at single-quantum relaxation. However, to my knowledge, the efficiency of this reaction has not been measured in the laboratory, mainly because the major interest was to know the relaxation of OH(v) and not where the energy goes. Are these reasons enough for completely disregarding the multi-quantum? I do not think so. The mechanism the authors propose sounds plausible but one should be careful about assuring that it is "the" mechanism (and reject the LP04 mechanism). If still the authors would like to be categorical, I think this point needs to be discussed deeper in the manuscript.

Page 3.

Minor comment. Lines 1-2. The proposed new mechanism strictly refers to OH(v) to N2(1), rather than OH(v) to CO2(v3).

Lines 5-6. "Kalogerakis et al. (2016) provided a definitive laboratory confirmation for the validity of this new mechanism." Were they able to measure the reaction rate and energy efficiency of this mechanism? Is this new mechanism still based on the "theoretical" calculations of Sharma et al. (2015) for the reaction rate of the OH(v)+O(3P)=> OH(v')+O(1D) ?

Lines 7-8. If the author would like to be consistent with the model of LP04 they should use the efficiency of 2.8-3.

Line 8. "... OH(v) energy transfer to "N2(1)" instead of to "CO2".

Lines 19. Again, in order to be consistent with LP04 the authors should use an efficiency of 2.8-3.

Lines 25-27. The SABER data version should be stated.

Line 27. As the authors mentioned above CO2 has been retrieved. I was then expecting to use the retrieved CO2 instead of that of WACCM. This should give better

simulated radiances and remove some uncertainties.

Reactions R1-R4 are repeated in the text and in the Table. Maybe they should be kept only in the Table.

Page 4.

Sec. 2.2

A major comment. As the new proposed mechanism affects also to the population of OH(v) and the emissions from these levels were measured by SABER in two different channels, I think it is essential that the authors demonstrate that the new OH(v) model explain very well the measured SABER OH radiances, as LP04 did. Thus, figures should be presented for different conditions comparing SABER observations and modelled radiances for the two OH SABER channels.

About the O(3P) abundance and the OH(v) model, the authors state that they used the O(3P) retrieved from SABER measurements. The SABER O(3P) is derived from the SABER OH radiances but a photochemical OH(v) model is required for such inversion (Mlynczak et al., 2013). How do the reaction rates for the OH(v) model used here (Table 1) compare to those of Mlynczak et al., 2013? Actually, to be consistent, it should be used the same photochemical OH(v) model in both cases.

Along this line, the mechanism proposed by LP04 did not affect the established OH(v) model (e.g. Adler-Golden et al., 1997), so in that sense it was also compatible with most of previous OH(v) emission rocket measurements. How does the new OH(v) photochemical model compare to that of Adler-Golden et al.? I.e., it is also compatible with previous OH(v) emission rocket measurements?

Line 9. The text in this line is repeated a few lines below.

Lines 14-15. Could the authors be more precise with "lower" and "higher" CO2 vibrational levels?

Line 21. Then the values used for the reaction rate of the new mechanism are based on theoretical estimations? not measured values? Kalogerakis et al. (2016) did not measure those the reaction rates and efficiencies? If measured, why not use the measurements with their errors instead of theoretical estimates?

Page 5. Sec. 3.2 Lines 20-25. This section and Fig. 2, when the authors refer to the calculations of LP04 with the "direct" mechanism, can be misleading. LP04 were able to reproduce the observed SABER radiances when using this mechanism but with an efficiency of 2.8.

"... inputs identical to those of Lopez-Puertas et al (2004)." Lopez-Puertas et al (2004) used version 1.03 of SABER parameters. Which version has been used here? Are they really identical? To which degree?

Lines 25 and ff. Using OH densities from WACCM. I believe the authors mean OH(v) densities, i.e. vibrationally excited OH, not OH in the ground state. In this case, the WACCM OH(v) densities might be largely under-predicted since it is well known that WACCM mesospheric O3 abundance is underestimated by at least a factor of 2 with respect to satellite measurements (both SABER and MIPAS) (Smith et al., 2013). By the way, the authors describe the OH(v) photochemical and the sources of some atmospheric constituents but not the source of O3 and H. Or was it included OH(v) (instead of OH) from WACCM and the OH photochemical model described (Table 1) is that of WACCM?

Page 7. Conclusions.

Lines 16-17: "This significant improvement suggests that the missing night-time mechanism of CO2(v3) pumping has finally been identified. " I would not be so categorical. At least experimentally it has not yet been ruled out the possibility of multi-quantum energy transfer from OH(v) to N2(1).

"Relevant laboratory measurements and theoretical calculations are sorely needed to

understand these relaxation rates and the quantitative details of the applicable mechanistic pathways." I understood from this manuscript that these have been already done (e.g. Sharma et al., 2015 and Kalogerakis et al. (2016). What new is needed?

"Nevertheless, results presented here clearly demonstrate significant progress in understanding the generation mechanisms of the night-time CO2 4.3 μm emission and represent an important step towards developing the algorithm(s) suitable for retrieving CO2 densities in the MLT from the SABER night-time limb radiances." I agree with the first part of the sentence. However, I see no real progress for an eventual retrieval of CO2 from night-time radiances. SABER measurements were already reproduced before as good as with this new mechanism. Further, even with such a good reproduction, the inversion of CO2 from night-time 4.3 μm emission in the regions where it would be useful (winter polar night) is still very difficult due to the reasons mentioned above.

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