We thank the reviewer for careful reading of the manuscript and helpful suggestions that lead to an improvement of the text. Here we reproduce referee's comments in full in italic and show our replies. Similarly, in the manuscript we use bold font to clearly denote the changed text.

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.

Response to general comment

There appears to be some confusion regarding the manuscript of Lopez-Puertas et al. (LP04) and its findings. The referee keeps making references to an unspecified multi-quantum alternative mechanism of LP04. Because of the plethora of “alternative facts” these days, it seems most appropriate to revisit the statements of LP04 (direct quotations from LP04 in boldface italics).

This is how LP04 summarize the findings or that study in the abstract:

"…We have investigated the SABER 4.3 μm radiances with the help of a non-LTE radiative transfer model for CO_2 and found that the large radiances can be explained by a fast and efficient energy transfer rate from OH(v) to N_2(1) to $CO_2(v_3)$, whereby, on average, 2.8–3 N_2(1) vibrational quanta are excited after quenching of one OH(v) molecule. A series of alternative excitation mechanisms that may enhance the nighttime 4.3 μm limb radiance were considered and found to be insignificant. <u>The mechanism(s) whereby the energy is transferred from OH(v) to N_2(v) is (are) still uncertain</u>…"

And below is an excerpt from the conclusions of LP04:
"…The indirect contribution of OH(v) through vibrational relaxation to N_2 and subsequent transfer to CO_2(v3) significantly enhances the CO_2 4.3 mm limb radiance in and everywhere above the upper mesosphere. However, the energy transfer estimated from the currently accepted quenching rates of OH(v) by N_2 is not enough to explain the large SABER radiances. <u>An energy transfer from OH(v) to N_2 that is more efficient than currently assumed, whereby a single N_2(1) molecule is excited after the relaxation of any OH(v) level, is required to explain the 4.3 μm radiance.</u> On average, about 2.8 – 3 N_2(1) molecules per OH(v) molecule are required to explain the SABER radiances.

There is no alternative mechanism presented in any detail in LP04. The important contribution of the LP04 study is that it examined in detail all the excitation mechanisms known at that time and, after determining that all these were inadequate, the LP04 study quantified the energy transfer rate that would be required to account for the discrepancies between model calculations and observations. Nevertheless, no detailed mechanism was described in LP04, let alone validated or justified by referring to any relevant theoretical or experimental investigations. As the quotes above show clearly, LP04 concluded that the nature of the active energy transfer mechanism was not known at that time. We suggest the referee read more carefully the LP04 paper so as not to misrepresent the important contributions of that study.

We agree with the referee that this manuscript "*represents an important research finding that deserves to be published.*"

Specific comments

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.

Our title does not state that we are"*reproducing SABER 4.3 μm observations*"-. We only say that "new model calculations improve agreement with SABER observations".

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.

The reviewer obviously means here that "*the results shown by LP04 in their Fig. 12*" obtained for some selected scans using the efficiency factor f=3 for the N2(1) production in the "direct" mechanism. *LP04* showed that using this factor as a fitting parameter removes about 40% of differences for these particular scans. We, however, showed in this study that for various latitudes/seasons the differences

between measured and modeled radiances, when f=1 is applied, reach up to 80%. These large differences can be reduced by using values of f=6 and higher. This kind of arbitrary fitting, however, is not needed anymore, when the new "indirect" mechanism is added to the standard one by Kumer (with f=1): working together both mechanisms provide reliable agreement for the large variety of atmospheric conditions. ***This reviewer obviously does not see this qualitatively new situation*** and persistently returns to this point many times in his/her report.

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%.

LP04 precisely formulated this puzzle: "***<u>An energy transfer from OH(υ) to N_2 that is more efficient than currently assumed is required to explain the 4.3 μm radiance"</u>***.
It actually took 11 years before a new efficient mechanism was found. Was it not a really long lasting puzzle? (even this statement neglects the fact that the puzzle started with Kumer as far back as the 1970s).

I would be more in favour of a title like "A new alternative mechanism for explaining the mesospheric night-time 4.3 μm emission" …

An "alternative mechanism" means that the problem can be explained by one or another way. Following persistent return of the referee to this point we will show below that the new mechanism leaves little room for alternative explanations. Does the reviewer suggest that after a new mechanism has been identified and validated, we simply forget about it? We have nothing against alternative explanations that will be shown to improve upon the new efficient energy transfer.

...or even been being more precise, for explaining the mesospheric night-time excitation of N2(1)".

Most of the authors have worked for many years with the analysis of SABER measurements (trying to resolving this and other "puzzles" related to these observations). We believe the title, which states improved agreement between SABER measurements and modeling is more accurate than the more academic "*night-time excitation of N2(1)"*. Therefore, we prefer to keep our current tittle, however, added in the conclusion words about the progress in "*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.

Following this advice, we changed the text in the paper body. However, in the abstract we simply want to let the reader know that we study the transfer of the OH(v) vibrational energy to CO2 and further to 4.3 μm emission. We, therefore, prefer to keep here the reaction chain as it is. Meanwhile, Kumer at al 1978 put the same reaction chain even in that paper title.

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 under-prediction (by up to 80%) of observed 4.3 μm limb radiances."

Following this comment, we changed the text of the abstract. We write now "However, accounting for this excitation mechanism (**with the currently accepted efficiency**) alone leads ..."

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.

Please see our discussion below about possible *multi-quantum* nature of these mechanisms. Relying on it we do not see the reasons to re-write this sentence.

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.

Above, we reproduced the LP04 conclusions. The final conclusion of that previous study was emphasized as a need for a more efficient mechanism, which we believe has finally been found. Following this comment we tried to make the paper text more consistent.

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.

The same statements about an "altenative mechanism" is repeated here.
Again, as we have already stated above, we have a completely different opinion. We believe we provided enough evidence that a new mechanism, which unfortunately was not known at the time of LP04, brings the situation regarding modeling of 4.3 μm night-time radiance at a qualitatively new level (see also discussion below).

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.

The reviewer is obviously in a different situation than most of us are. Some co-authors of this manuscript are directly funded from the SABER/TIMED experiment and, therefore, it is our job to search for new mechanisms, which can improve the interpretation SABER measurements. We consider this study as an important first step toward developing new algorithms for CO2 retrieval from the night-time 4.3 μm SABER signals.

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, ….

We agree with the referee that the new mechanism is important.

… 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 referee suppose that knowing daytime CO2 guarantees its accurate prediction for night-time, or makes the night-time retrievals not important and, therefore, not needed. However, this is just a guess of this referee, which is not confirmed by any observations. However, Nature is continuously demonstrating that it is much more inventive than our guesses, therefore, it may easily happen that nighttime CO2 is different, and, since CO2 (so far, that of WACCM) is used for temperature retrievals from the 15 μm emission, then temperature/pressure will be also different from those predicted by the model, and so on. Additionally, does the referee suggest to just simply forget about significant fraction of SABER observations collected during the last 15 years?

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.

The reviewer continues here with his/her strange way of thinking: the polar night is the complex region, and what? Should we better forget about it and find another object of research?

And last, the night-time 4.3μm signal is usually much more noisy (~a factor for 100 or larger) than the daytime one.

We agree with the reviewer regarding the reduction in the absolute value of the nighttime CO2 radiances relative to the daytime (~100 smaller). However, the NER for the SABER Ch7 is ~ 1e-6 W/M2/Sr, (see, for instance, Mertens et al, 2003). However, the nighttime Ch7 radiances are still roughly a factor of 5 higher than NER for large number of scans up to 115-120 km, see the plots at the end of this document, which show fractions of our analysis of the Ch7 signals (in W/M2/Sr), version 2.0, versus solar zenith angle. There are many profiles that have SNR >100 at 115 km, which is an interesting effect on its own, but also implies the retrieval could proceed to 120-130 km. It also implies that the nighttime retrieval will have a moving upper boundary, but it may proceed without issues at least up to 100-110km, and in some instances up to 120-130 km.

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.

This is another return to the same idea about equal importance of both new and old mechanisms. Please see our replies above (and also below).

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.

This is again the same topic. Please see more detail discussion below. Briefly: we do not completely disregard the "old mechanism," but we cannot accept it (with a thus far unexplained arbitrary efficiency of ~ 3) as an equivalent alternative to the new mechanism. Nevertheless, we changed the text from "instead of the accepted value of 1" to "instead of the currently accepted value of 1"

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.

We are not "categorical" at all, although we could be more categorical relying on our justifications: (a) the efficiency of the new mechanism is justified with detailed theoretical and laboratory analysis by Sharma et al 2015, and Kalogerakis et al, 2016, and (b) our study shows that the new mechanism leaves little space for other "alternatives".

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

We made the corresponding correction in the text.

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) ?

Please see detailed discussion of the same comment below

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.

Once again, we state here that we do not study the ability of the Kumer mechanism to fit SABER measurements testing a hypothetical higher efficiency. Our goal is different – to show the effect of a

newly discovered and validated mechanism when it works together with that of Kumer, which is used with the currently accepted efficiency of f=1.

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

We changed the text.

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

Please see our replies above.

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

We used 2.0 version and added this information to the text

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.

What kind of “some uncertainties” does the referee mean? Our main conclusion is quite certain – the new mechanism is important and must be accounted for. Using retrieved daytime CO2 (which, meanwhile, is still not publicly available) will not change this conclusion.

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

We would prefer to show reactions in both text and table. It will be easier for readers not to be referred to the table multiple times when the various mechanisms are discussed.

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.

The referee is raising a good point that we considered in our consistency checks by evaluating the effect on the OH(v) population for the two highest vibrational levels. We found very good agreement (within a few percent) between the number density determined for OH(8+9) from our test data sets and the SABER channel 8 observations. The absolute number density for OH(8+9) can be directly determined from the SABER Channel 8 radiances (Mast et al., 2013) and is therefore a rigorous consistency check. The extracted OH(8+9) absolute number density does not depend on any previous model result (only the radiance profile and the almost equal Einstein emission coefficients A97 and A86 are needed). Our ultimate goal is to develop an updated model that handles simultaneously all the SABER OH(v) and CO2 emission channels, but this is clearly out of the scope of this report. The goal of our study was to estimate, with the help of model calculations that are based on reliable inputs, the

effect of the recently discovered “indirect” pumping mechanism of N2(v) at nighttime. The latter was suggested and then experimentally confirmed by Sharma et al, 2015 and Kalogerakis et al, 2016, respectively. We believe we demonstrated the importance of this new mechanism and made significant contributions that complement the previous studies. Nevertheless, as we make clear in our conclusion statements, there is plenty of room for further research.

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.

We took as much information as possible (pressure, temperature, O, O3, H) from SABER retrievals. However total OH density was taken from WACCM to calculate OH(v) following the model similar to that described by Xu et al (2012). We repeat again here that our goal was quite limited – to estimate with the help of reliable model calculations the effect of the new N2 pumping mechanism at nighttime.

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?

Please see our comments above about OH(v) comparisons.

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

We changed the text.

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

In the majority of cases the rate coefficients are measured/calculated only for transitions between ground and first excited vibrational levels (in some cases between lower nearby lying vibrational levels). Shved at al 1998 suggested scaling these values to similar transitions between higher vibrational levels. We applied these scaling rules in our CO2 non-LTE model.

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?

The estimate for the total removal rate constant for OH(v = 9) + O at mesospheric temperatures, 3e-10 cm3 s-1, is based on laboratory experiments conducted at SRI International: Kalogerakis et al. (2011) investigated OH(v = 9) + O at room temperature and Thiebaud et al. (2010) reported the

temperature dependence of OH(v = 7) + O from room temperature to mesospheric temperatures, assuming that these processes have similar temperature dependence. Sharma et al. (2015) estimated the rate constant for the OH(v = 9) + O multi-quantum vibrational relaxation pathway leading to O(1D) excitation by subtracting from the total removal rate constant the contributions of inelastic vibrational relaxation and reaction to H + O2, as calculated by Varandas (2004). The corresponding rate constant estimates are 3.2e-10 cm3 s-1 and 2.3e-10 cm3 s-1 at room temperature and at temperatures near 200 K, respectively. The laboratory experiments by Kalogerakis et al. (2016) confirmed the prediction of Sharma et al. (2015) at room temperature. Therefore, the rescaled rate constant for the multi-quantum vibrational relaxation pathway used in the modeling calculations reported here also relies on the experimentally measured temperature dependence for OH(v = 7) removal by O atoms. Rescaling of available OH(v) + M rate constant values is common practice when measurements at the temperature of interest are not available in the literature (e.g., Adler-Golden, 1997; LP04). The reviewer can find more detailed discussion in the papers by Sharma et al, 2015 and Kalogerakis et al, 2016. We also changed the manuscript text to refer readers to both papers.

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.

To avoid possible misunderstanding, we changed here the text from "... (R1-R3) only (``direct" mechanism)" to "..(R1-R3) only ("direct" mechanism with currently accepted efficiency 1)"

"... 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?

We used version 2.0. Version 1.03 which was used by LP04, is no more available, therefore, it was impossible to rigorously compare LP04 and our model inputs. That was not our goal, to literally reproduce the LP04 results, which we show just for comparison, however, we mention that both simulated signals (for the currently accepted efficiency of Kumer mechanism) are very close. These two signals, as well as other simulated signals are compared to the measured signal from the current 2.0 version. Digitizing the Ch7 signal shown by LP04 and comparing it with the signal currently available for the same scan we found a small difference reaching maximum of 10% around 70 km, which are not important for comparisons discussed in our paper.

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?

In our reply to RC1 to similar comments we stated (and also changed the manuscript text) that we used in these model calculations O3, H and O retrieved from SABER, but **total**

OH density was taken from WACCM, and OH(v) we calculated with our own non-LTE model.

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).

N2 is still considered as quite an in-efficient quencher of OH(v), see discussions by Kumer et al 1978, Burtt and Sharma, 2008 and Sharma et al, 2015, and references therein. It has never been shown and is still not expected that a process of the type OH(v) + N2(0) --> OH(v-n) + N2(k), where n and k > 1, would have any significant probability. Additionally, (a) the verb "suggests" we used is certainly not categorical. Moreover, our confidence is based on the fact that new mechanism accounts for most of the discrepancy, thus it appears there is little room for other processes (that, of course, cannot be excluded, but are not expected to be significant), (b) everything else that follows in our conclusions is rather measured and does not claim that we know everything: "Further improvements will require optimizing the set of rate coefficients used for OH(v) relaxation by O(3P) and O2 at mesospheric temperatures and, in particular, understanding the dependence of the indirect mechanism on the OH vibrational level. Relevant laboratory measurements and theoretical calculations are sorely needed to understand these relaxation rates and the quantitative details of the applicable mechanistic pathways."

"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?

Please see the reply to previous comment.

"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.

We appreciate this at least “partial” agreement with our conclusions.

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.

Summarizing all discussion above, we once again draw the referee’s attention to the following:

- LP04 showed that Kumer mechanism with f=1 in no way reproduces measurements. Even for very carefully selected scans the differences reached 40%

- LP04 also showed that f=~3 (possible multi-quantum process, but mechanism is not explained) removes about 40% of differences for some selected scans studied. In our very extensive study we found that these differences can reach as high as 80%. Following the LP04 logic it would

require f=6 and higher to remove these differences, which is absolutely unrealistic. In other words, LP04 quantified the energy transfer efficiency that would be required for model calculations and observations to agree (for some limited set of scans), but no detailed mechanism was described, let alone validated by referring to theoretical or experimental investigations.

- Sharma et al 2015 in a detailed analysis suggested a new efficient mechanism of transferring OH(v) energy to N2(v), and Kalogerakis et al 2016 demonstrated the validity of this hypothesis in laboratory experiments. As we showed in our extensive study the new Sharma mechanism (combined with that of Kumer for f=1) very efficiently removed up to 80% of signal differences for the large variety of atmospheric situations.

- The new mechanism leaves little room for other processes (that, of course, cannot be excluded, but are not expected to be significant at this point, and will need to be validated first theoretically or experimentally, or better yet in both ways, just as in the case of the Sharma mechanism).

- This referee agrees that Sharma's et al., Kalogerakis' et al., and our results "*demonstrate significant progress in understanding the generation mechanisms of the night-time CO2 4.3 μm emission"*

- Progress in understating observed phenomena is usually followed by practical or technical application of this new understanding, which, in our case, will be the retrieval algorithm. We invite the referee and his/her group to make their own research contributions, given the new knowledge.

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.

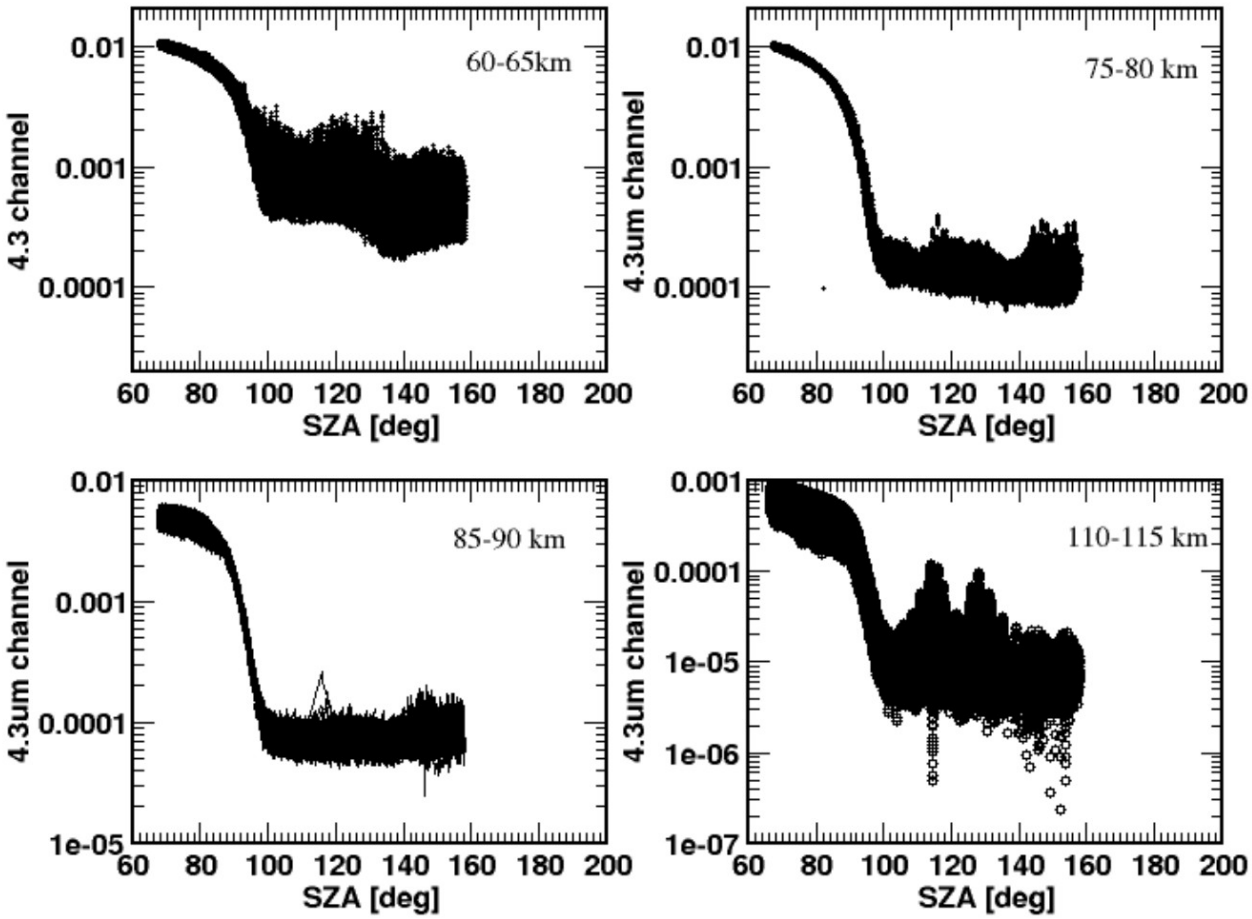
Please see our reply to the same comment above.

References

Burtt, K. D. and Sharma, R. D.: Near-resonant energy transfer from vibrationally excited OH to N2, J. Chem. Phys., 128, 124311, doi:10.1063/1.2884343, 2008.

Mast, J., M. G. Mlynczak, L. A. Hunt, B. T. Marshall, C. J. Mertens, J. M. Russell III, R. E. Thompson, and L. L. Gordley (2013), Absolute concentrations of highly vibrationally excited OH(õ = 9 + 8) in the mesopause region derived from the TIMED/SABER instrument, Geophys. Res. Lett., 40, 646–650, doi:10.1002/grl.50167.

2002, 121-125


60-65km
75-80 km
85-90 km
110-115 km
4.3 channel
4.3um channel
SZA [deg]
0.01
0.001
0.0001
1e-05
1e-06
1e-07
60
80
100
120
140
160
180
200

Jan 1-15, 2003