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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric Band Fitting Coefficients Derived from Self-Consistent Rocket-Borne Experiment" *by* Mykhaylo Grygalashvyly et al.

Anonymous Referee #1

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Second Referee's comments on manuscript Number: acp-2018-696 Title: Atmospheric Band Fitting Coefficients Derived from Self-Consistent Rocket-Borne Experiment Author(s): Mykhaylo Grygalashvyly et al.

This paper try to confirm the chemical production processes responsible of the Atmospheric Oxygen emission observed in the Earth nightglow. Although previous works have pointed out that the excited state of molecular oxygen O2(b), responsible of this emission, is produced mainly by a transfer recombination processes, because, with the available information up to now, direct recombination of atomic oxygen process, alone, can not explain the amount of emission measured in many different experimental at-

mospheric airglow measurements, it is the first time that are available simultaneous measurements of the main parameters involved in the chemistry of O2(b) state: O2(b) Atmospheric emission profile, atomic oxygen, temperature, atmospheric density... and this offers the opportunity to check and improve our knowledge of the O2(b) chemistry.

This is the main goal of this study, the opportunity of using simultaneous measurements of all the parameters involved in the O2(b) chemistry to perform this investigation.

The main conclusions derived are: A total efficiency for O2(b) production of 0.10 in a transfer mechanism (close to the previous accepted values) with a quenching ratio for the precursor Ko/Ko2 of 0.21 (10-20 times smaller than the previous accepted values). These results are what have to be analysed with care and discussed. Although the authors have answered some of my previous comments, I think sometimes the authors lose the focus of work, and do many speculative work on some aspects that do not lead to any new conclusion.

First, I do not consider necessary many of the analysis devoted to atomic oxygen direct recombination process. So Figures 2 and 3, and many of the discussion refereed to them, should not be here. Once the authors obtain from direct recombination analysis that an efficiency of 0.07-0.13 is required for O2(b) production means that this process, alone, can not explain O2(b) production, following theoretical and experimental previous works (as it is said many times along the text and supported by references), then, all additional the work of considering only direct recombination process and possible dependences of the efficiency with temperature and pressure is very speculative, first because of the large value of this efficiency and second because in the altitude range of the atmospheric region considered ($\sim$10km) there is not large variation of temperature and pressure condition (although they could reach +-50K and/or a few micro bars). This is an exercise and it confuses and makes lose the focus of the work.

So Figure 2 and Figure 3 are not needed.

Figure 4, 5 and 7 need some improvements:

1) Plot some subintervals in the vertical and horizontal axes.

2) There are points (data) only at about each 3 km. Points at each 1 km should be shown, although the error bars be shown only each 3 km.

3) Figure 3 shows very good fit between about 97 and 98 km (as I can guess in figure 3 without any subdivision!). It will be interesting to show in the same figure the temperature profile (with and appropriate temperature scale in the upper horizontal axis), and the number density to see how the structure of temperature and number density can affect the fitting.

I think that the authors still should make additional work, to support these results.

I have made a few recommendations (see details that follows):

Abstract

Line 19- 20: ",we derived the empirical fitting coefficients,....(0,0) in terms of the atomic oxygen concentrations." Delete "in terms of the atomic oxygen concentrations" To read: ",we derived the empirical fitting coefficients,....(0,0)."

Line 25: "Simultaneous and true common volume measurements of all the parameters used in this derivation, i.e...." Change to: Simultaneous measurements of all the parameters involved in the theoretical calculation of the observed O2(b) emission, i.e...."

Introduction:

Line 33-35 Change: "particularly, by emissions in the Atmospheric Band that form the excited state of molecular oxygen O2(b)..." To read " particularly, by the emission of the Atmospheric Band which is produced by the emission of the excited state of molecular oxygen O2(b)..."

Lines39-40 Change "Lopez-Gonzales" to "Lopez-Gonzalez"

Line 66 Delete "O or"

Line 67 Change "by known" To read "and"

Line 67 add "values" to read " volume emission values"

Line 70 change "leads to the loss of self-consistency (e.g Murtagh et al., 1990)." To read "leads to some degree of uncertainty (e.g Murtagh et al., 1990)."

Line 70-71. Delete "and, consequently, to essential biases." To read "(e.g Murtagh et al., 1990)."

Line 73-74 Delete " real common volume in-situ measurements of these..." To read: "simultaneous measurements of these..."

Line 75-79 Change "chapter" To read "section"

2. Rocket experiment description

Here I have a question, it is described that FIPEX use two types of solid electrolyte sensors platinum electrodes sensitive to both molecular and atomic oxygen, whilst gold electrodes show a selective sensitivity to atomic oxygen. Is this mean that it can measure molecular oxygen too? If it is possible, It would be useful this O2 profile were shown in the plot.

3. Theory

All this section is just a very detailed recompilation of the known mathematical expressions used in O2b calculations. There are too many details that should be reduced.

I think expression (2) should be deleted is already said in line 135-136 (same that equation 1).

Then expression (4) and (5) should be deleted and put only expression (6). Then delete expression (7), it is not needed, and write expression (8).

Then (1),(3), (6) and (8) expressions could be written, to easy understand the "nomenclature".

4. Results and Discussion:

Comment: Figure 1, shows atmospheric concentration, [N], temperature, T, atomic oxygen concentration, [O], and Volume emission rate. Here Figures 1b) and 1c) should have additional subintervals in the logarithmic x axis. Additionally molecular oxygen concentration is used in the analysis performed. I have a question what values of O2 are used? (is there some additional measurement from FIPEX?, or are derived from the measurements of [N] (density) and [O]?)

Question: Lines 174-177. It said: "Our rocket experiment shows an essential difference of emissions between ascending and descending flights (see Strelnikov et al., 2018). It also demonstrates a significant variability in other measured parameters, including neutral temperature and density as well as atomic oxygen density."

How large is this difference? The time between ascending and descending flights should be a very few minutes. Perhaps it could be interesting to show the profiles of the different parameters obtained in both, the ascending and descending, flights to see these differences.

4.1 On-step mechanism.

This subsection has to be very simplified. There is a lot of speculative exercise that leads to any point.

For example: The efficiency calculated by using direct atomic oxygen recombination for the production of O2b to explain the observed emission, is in the range of about 0.07-0.13, this value is too large compare with the obtained by laboratory and theoretical investigation (Wraight, 1982; Ogryzlo et al., 1984; Bates, 1988). Then, direct atomic oxygen recombination alone can not explain the observed emission in agreement with earlier works (McDade et al., 1986; Bates, 1988;...)

Any other exercise is not necessary. So figure 2 y 3 should be deleted.

4.2 Two step mechanism.

Figure 4. Please, put some subintervals specially in the y axis. Here I see a very good fitted region of about 97-98 km (as I guess because of the lack of subintervals!), and important deviation of the fit above and below this region. I think it would be interesting to show, simultaneously in the figure, T profile (with a horizontal scale from 150K to 210K, in the upper x axis) and the N profile (the same scale as RHS Eq.8, in the lower x axis, is appropriated) to easy see how temperature and atmospheric density profiles affect to the features observed in RHS equation 8.

Line 259: Delete "s" to read " and molecular oxygen"

Line 261: Change "are 3.1 and 2.9" to read "of 3.1 and 2.9"

Line 282-283 Change "we show Figure 5 with atomic oxygen concentration from... " To read "we compare in Figure 5 the atomic oxygen concentration from ..."

((Figure 5 and Figure 7 need to show subintervals in both axes (vertical and horizontal), also the data points should be plotted each 1 km.))

4.3 Combined mechanism

Figure 6 is not necessary, all the information is in table 3.

I do not think to put the equation (9) is needed. Neither do I consider an appendix necessary. So I will deleted the appendix and will reduce the equation 9 and the explanations to: "... we have investigated a combined mechanism of direct and indirect atomic oxygen recombination, the fitting coefficients for the transfer energy process were calculated for.... The results for the best-fit in each case are listed in Table 3." (Now in Table 3 only K3o/k3o2 and total efficiency would shown (delete D1 and D2))

Line 305-310 Delete all.. "They are listed in Table 3. The altitude profile of the RHS of equation (9) and calculated fit-function are plotted in Figure 6. The deviations of fit function between limits and averaged values are negligible, hence, we only show the averaged case. Thus, we can recommend for future investigations the values of averaged case (last column of Tab. 3). Analogously to the two-step mechanism....<1.

Taking into..." To read: "The results for the best-fit in each case are listed in Table 3. Taking into..."

LIne 311. Add (see Table 3) to read "0.073 (see Table 3)."

Line 327-330. Delete this sentence "Note that... two point, respectively." It is not needed.

Line 330-332. Rewrite this sentence. For example: The total efficiency of production of O2b through an energy transfer process and new coefficients derived in this work provide a valuable information about the chemistry of O2b. Moreover, the importance of make studies with the possibility of using simultaneous measurements is strongly pointed out.

Conclusion:

This section has to be very summarised. There is a long text, and here the results has to be clearly established.

Line 336: Change "true common volume observations" to read "simultaneous observations"

Line 337-338 "delete one-step. two step and combined" to read "the mechanism of o2b formation were analysed".

The following discussion for one-step and two-step should be deleted. These are from line 339 to 356. Only the proposed mechanism should be mentioned.

Line 357-360 are when the main result are reflected. This can be rewritten as: Based on simultaneous observations of atomic oxygen, atmospheric band emission (762 nm), and density and temperature of the background atmosphere and all the information available up to now about reaction rates coefficients, branching ratios, quenching rates and spontaneous emission coefficients the mechanism of o2b formation were analysed.

A direct and indirect atomic oxygen recombination process to explain the production of O2(b) is the one chosen as responsible of the atmospheric emission observed. The total efficiency of production of O2b in the indirect recombination process is of 0.08 and the ratio of quenching coefficient of the precursor state is 0.231, when an efficiency of 0.02 in direct recombination is chosen. The analysis of the values of the total production indicates that O2A' or O2Pi may be possible precursors for the two-step mechanism.

The lines 361-366 reflect the final thoughts, so here Lines 361-366 ramble on about these mechanisms again in a confused way. Instead, it should show the need to make simultaneous measurements to confirm and improve these results.

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