

Interactive comment on “Photochemical modeling of molecular and atomic oxygen based on multiple *in-situ* emissions measured during the Energy Transfer in the Oxygen Nightglow rocket campaign” by Olexandr Lednyts’kyy and Christian von Savigny

Olexandr Lednyts’kyy and Christian von Savigny

olexandr.lednytskyy@uni-greifswald.de

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Response regarding comments of the Anonymous Referee #2 on acp-2019-221: Photochemical modeling of molecular and atomic oxygen based on multiple *in-situ* emissions measured during the Energy Transfer in the Oxygen Nightglow rocket campaign

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Comments of the Anonymous Referee #2

Feedback to the pdf-paper:

I believe that this paper contains a valuable contribution to the field and as such is publishable. However the paper is extremely difficult to read and requires major revision of the structure and language before it can be published.

General comments to the pdf-paper:

The paper is attempting a complex task and may be helped by some flow charts show in the procedures, the relationships between various products etc.

As I have managed to understand the paper: The authors first review a substantial literature on many of the airglow emissions contrasting and comparing relevant groups and then make selections as to which reactions to maintain in the MAC model.

List of corrections regarding general comments of the Anonymous Referee #2

The authors of the manuscript are grateful to the Anonymous Referee #2 for the general comments. We agree that the paper was difficult to follow. We edited the paper and changed the text substantially. The paper is now hopefully easier to follow. Also, following the reviewer’s suggestion a flow chart was added as Fig. A1. Changes in the manuscript were highlighted by bold font.

Page 37, line 14, regarding the new third paragraph:

Retrieval steps resulting in $[O(^3P)]$ and carried out according to the proposed algorithm are illustrated in the flow chart in Fig. A1.

Additionally, the new Fig. A1 was added on page 37. The figure is saved as the supplement file acp-2019-221-AC2-supplement.pdf. Text of the figure caption is as follows:

The flow chart shows retrieval steps resulting in $[O(^3P)]$ and carried out according to

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the proposed MAC approach. The start and end states are denoted by filled black circles on the top and bottom of the figure, respectively. Decisions and processes are denoted by rhombs and rectangles, respectively. Connectors are denoted by empty circles. The flow chart is read following lines with arrows from one flow chart symbol to another. The prior retrieval procedure is described by the text shown in blue. If the prior retrieval procedure can be omitted (as it is the case for the ETON campaign), then the corresponding decision “Not important” (shown in violet) near a rhomb is to be taken that is denoted by “optionally” (shown in violet in a rectangle) being relevant for the optional calculation result (shown in blue in a rectangle). The optional procedure carried out to retrieve $[O_2(A)]$ and $[O_2(A')]$ is described by the text shown in green. If emissions in the Herzberg I and Chamberlain bands are not available (see “No” shown in violet near the respective rhombs) or optional (see “Not important” shown in violet near the respective rhombs), then this optional procedure can be omitted at steps 2.3 and 3.1, see $[O_2(A)]$ and $[O_2(A')]$ shown in green in the respective rectangles. Note that the $[O(^3P)]$ retrieval can be carried out most accurately if values of $VER\{O_2(b-X)\}$ are available which is indicated by the text shown in red.

Additionally, the following relevant change was carried out in Table 9 on page 56, Table 10 on page 57, Table 11 on page 58, Table 12 on page 59 and Table A1 on page 60. These tables were sorted and placed not after the bibliography as was done earlier, but in the respective sections.

Additionally, the following relevant change was carried out in Table 12 on page 27:

The content of Table 12 was revised and compressed representing concentrations of many excited species, e.g. $[O_2(A, A')]$ instead of $[O_2(A)], [O_2(A')]$ and so on. Note that this change was not highlighted.

Additionally, the following relevant change was carried out in Table 7 on page C3

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... $R_{s2.1-6}$...
was changed to:
 ... $R_{s2.1-3} \dots R_{s2.4-6}$...

List of corrections regarding specific comments of the Anonymous Referee #2

The authors of the manuscript are grateful to the Anonymous Referee #2 for the specific comments. The manuscript was substantially revised and the english has been hopefully improved. We hope that the paper is now easier to follow. Changes in the manuscript were highlighted by bold font.

Specific comment:

Some tests are then carried out but I was unable to follow exactly what was done. I believe that Figure 3 is supposed to show the agreement between the model after tuning with the various ETON emission profiles. I do not see the point in showing both the concentration of the emitter and the intensity of the emissions as the conversion between them is trivial.

Response:

Thank you for reminding about the triviality of the conversion between the concentration of the emitter and the intensity of the emissions. We would like to keep the text about this conversion in Appendix A describing steps in sections A2.1, A2.2, A2.3, A3.2 and A4.1. The corresponding consistency tests are described in Appendix A in Sections A2.4, A3.3 and A4.2. We would also like to keep both panels in Fig. 3 as the result of the carried out consistency tests. We substantiate our choice by the fact that Huang and George (2014) verified their calculations comparing concentration profiles

in their Fig. 1. Therefore, we also show concentration profiles in the right panel of our Fig. 3 to allow the comparison of calculation results shown by Huang and George (2014) in their Fig. 1 and our results shown in the right panel of our Fig. 3 easier, i.e. without additional calculations required for this conversion. In fact, the MAC model includes reactions proposed by Huang and George (2014) as well as many other reactions. Note that we employ updated reaction rate values considered by Huang and George (2014) in their Table 1. This makes the comparison of concentration profiles obtained by us and Huang and George (2014) necessary. Additionally, we compare VER profiles in the left panel of our Fig. 3 as was done by Murtagh et al. (1990).

Following your comment, the following relevant change was carried out in caption of Fig. 3 on page 23:

... are coherent with measurements. The abbreviations ...

was changed to:

... are coherent with measurements. The corresponding consistency tests are described in Sections A2.4, A3.3 and A4.2. Note that the conversion between profile values of VER and concentrations is based on trivial, but required calculations provided in Sections A2.1, A2.2, A2.3, A3.2 and A4.1. The abbreviations ...

Specific comment:

The sensitivity analysis in section 3.5 is a useful contribution. I might note that the temperature cannot actually be varied independently of the pressure because of hydrostatic equilibrium.

Response:

The reviewer is certainly correct that temperature and pressure are directly connected. However, it may occur that one of the two quantities is measured with a very high accuracy, and the other one is not. We would like to keep the sensitivity analysis considering the mentioned parameters, i.e. $[N_2]$ and $[O_2]$ (calculated using pressure)

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as well as temperature, separately because of two reasons. Firstly, instruments aboard the WADIS-2 rocket and the SABER instrument provided data required to obtain pressure and temperature. The sensitivity analysis carried out by Lednyts'kyy et al. (2019) is based on pressure and temperature considered independently from each other. The sensitivity analysis discussed in our Section 3.5 is carried out in a similar way as was done by Lednyts'kyy et al. (2019). Finally, the mentioned parameters are also considered independently from each other in the continuity equations employed here. In summary, we would like to keep the applicability of the sensitivity analysis because it contains more information than treating temperature and pressure in a combined way.

Specific comment:

Much of the content of section 4 - discussion should appear earlier in the paper to explain what is actually done in the model. For instance the tuning of parameters is described first in section 4.1.

The text on page 28, lines 12-17, was used to extend the text on page 14, line 32:

... states. It should be noted that ...

was changed to:

... states. In fact, the removal of the $O_2(^5\Pi)-O_2(A, A')$ -group through collisions was suggested by Slanger et al. (2004b) and implemented in the MAC model implicitly by increasing the association rates of $O_2(b, a, X)$ in the three-body recombination reactions. This was done implicitly because reactions including $O_2(^5\Pi)$ are not well known, e.g., compare Krasnopolksy (2011) and Krasnopolksy (1986). It should be noted that $O_2(^5\Pi)$ has a shorter lifetime and a higher energy compared to the other states $O_2(A, A', c, b, a, X)$ as it was also mentioned by Huestis (2002) and Slanger et al. (2004b). It should be noted that ...

Additionally, the following relevant change was carried out in the title of Section 4.1 on page 29, line 9:

Discussion of tuned rate values of quenching processes implemented in the MAC

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model.

was changed to:

Tuning rate values of quenching processes implemented in the MAC model.

Additionally, the text of Section 4.1 on pages 29 and 30 was written after Section 3.3 on page 16. Note that the added text was not highlighted.

Specific comment:

The discussion of dynamics on page 32 seems somewhat superfluous to the aim of the paper and could be excluded.

Response: The mentioned text on page 32, lines 16-21, and on page 5, lines 14-17, was deleted.

Additionally, the reference to Smith et al. (1987) on page 54, lines 19-21, was deleted. The reference to Johnson and Gottlieb (1973) on page 50, lines 17-18, was also deleted.

Specific comment:

The use of some wording also confuses the reader. I believe that the use of "continuity equation" in for instance line 9 page 32 refers to a steady state chemical balance equation although some wording earlier in the paper may suggest that time dependent equations are being solved.

Page 32, line 10:

Continuity equations implemented ...

was changed to:

Steady state chemical balance equations (also referred to as continuity equations) implemented ...

Additionally, a similar change was carried out on page 2, line 30:

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... the resulting mass conservation (continuity) equation ...

was changed to:

... the resulting steady state chemical balance equation (hereafter referred to as continuity equation) ...

Additionally, a similar change was carried out on page 37, line 6:

Then simple continuity equations ...

was changed to:

Then simple steady state chemical balance equations (referred to as continuity equations) ...

Specific comment:

The use of the word retrieve when I believe calculate would be better is also a problem.

Eg line 10 page 38, line 12 page 39.

The following change was carried out in titles of each subsection of the Appendix A (e.g. A2.1, A2.2, A2.3 and A2.4, but not A2) and for references in Appendix A to the mentioned sections:

... retrieval ...

was changed to (and highlighted in bold italic font):

... calculation ...

Specific comment:

A few minor points Page 4 line 22 - The reference to Greer et al 1986 about the atomic oxygen measurement technique would be better replaced but a reference to one of the Dickinson papers.

Page 4, line 30:

... at ~130 nm (Greer et al., 1986) and ...

was changed to:

... at ~130 nm (Dickinson et al., 1980) and ...

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Specific comment:

Page 12 second line of the caption to table 3. I believe it should be the character E that marks the equations excluded not M.

Page 5, line 2, caption of Table 3:

The processes marked with a character M are not considered ...
was changed to:

The processes marked with a character E are not considered ...

Specific comment:

Page 28. In the discussion of the vibrational distribution of the Herzberg states a reference to some of the ground based work by Slanger or Stegman might be appropriate.

Page 28, line 21:

... energetically very close to each other. Vibrational states ...

was changed to:

... energetically very close to each other. Vibronic energy levels of $O_2(A, A', c, b, a, X)$ are shown in Fig. 8 by Goodman and Brus (1977). The atlas of terrestrial nightglow emission lines in the range 314...1043 nm including emission lines of these O_2 states is provided in Table 3 as a compressed form of the electronic supplement of Cosby et al. (2006). Vibrational states ...

Additionally, the following relevant change was carried out on page 28, line 10:

... coupled with $O_2(c, b, a, X)$ which was also adopted in the MAC model.

was changed to:

... coupled with $O_2(c, b, a, X)$.

Discussion with C. von Savigny resulted in the following changes.

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The following change was carried out in Table 2 on page 8, Table 3 on page 12, Table 4 on page 13, Table 5 on page 17, Table 6 on page 18, Table 7 on page 19, and Table A1 on page 60:

... $h\nu($...

was changed to:

... $h\nu($...

Additionally, the following change was carried out on page 4, lines 19-20:

The maximal number of VER profiles related to various O_2 and $O(^3P)$ transitions were obtained by two ETON rockets, which are discussed here. As for the Infrared Atmospheric band emissions at $1.27\ \mu m$, they were measured ...

was changed to:

All VER profiles considered in the MAC model were measured during flights of two ETON rockets. The Infrared Atmospheric band emission at $1.27\ \mu m$ was measured ...

Additionally, the following change was carried out on page 11, lines 17-19:

In contrast to the YM2011 model, reaction rates in the modified kinetic model of Mlynczak et al. (1993) refer to a specific portion of vibrational states from their statistical equilibrium in each O_2 electronic state.

was changed to:

Rate values of reactions involving $O_2(b)$ and $O_2(a)$ in the modified kinetic model of Mlynczak et al. (1993) do not directly correspond to rate values of reactions involving various vibrational states of $O_2(b)$ and $O_2(a)$ in the YM2011 model because vibrational states are not identified in the modified kinetic model of Mlynczak et al. (1993).

Additionally, the following change was carried out on page 30, lines 9-10:

... the results of which are given by the interval of possible rate values shown in the third column of Tables 8...11.

was changed to:

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... see the third column of Tables 8, 9, 10 and 11 for a summary.

Additionally, the following change was carried out on page 28, lines 24-25:

Considering internuclear distances (INDs) of the corresponding Franck-Condon factors, it should be emphasized that the difference in INDs between the excited ... was changed to:

Considering Franck-Condon factors and the corresponding internuclear distances (INDs), it should be emphasized that the difference in INDs between the excited ...

Additionally, the following change was carried out on page 34, lines 30-32:

It is difficult to argue about the fractional $O_2(c)$ vibrational population of the $O(^1S)$ precursor because the $[O_2(c, \nu=6, 7, 8)]$ peak might be at about 97 km altitude if the collisional activation energy mentioned by Krasnopolsky (1981) is neglected.

was changed to:

In summary, the exact role of the vibrational excitation of $O_2(c)$ as a precursor of $O(^1S)$ is still not well understood and should be investigated in future studies.

Additionally, the following change was carried out on page 36, lines 19-21:

Then, the following correspondences among the violated electric dipole selection rules and the transition intensity seem to be established. ... (3) almost absent between $O_2(A^3\Sigma_u^+)$ and $O_2(A'^3\Delta_u)$ as well as $O_2(c^1\Sigma_u^-)$ and $O_2(a^1\Delta_g)$.

was changed to:

Then, the following correspondences regarding the selection rules for chemical reactions were established. ... (3) almost nearly absent between $O_2(A^3\Sigma_u^+)$ and $O_2(A'^3\Delta_u)$ as well as between $O_2(c^1\Sigma_u^-)$ and $O_2(a^1\Delta_g)$.

Additionally, the following change was carried out on page 40, lines 25-27:

This is justified because O_2 in these triplet excited states is decoupled from the singlet excited states according to the hypothesis of Slanger et al. (2004b) used to propose the MAC model, which were verified and validated, (see Section 3.5).

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was changed to:

This is justified because the hypothesis of Slanger et al. (2004b) was adopted to propose the MAC model. Note that the MAC calculations were verified and validated, see Section 3.5 for details.

Additionally, the following change was carried out on page 43, lines 24-25:

... was not retrieved on the basis of VER values, but concentrations available from the previous calculation steps.

was changed to:

... was retrieved on the basis of concentrations available from the previous calculation steps, whereas VER profiles were not employed for the $[O_2(c)]$ retrievals directly.

Additionally, discussion with C. von Savigny resulted in the update of references on page 48 line 10, page 51 line 10, page 51 line 16, page 51 line 18, and page 51 line 22.

Additionally, discussion with C. von Savigny resulted in numerous changes regarding English grammar and style. These relevant changes were carried out and highlighted in the manuscript.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2019-221/acp-2019-221-AC2-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-221>, 2019.