

Interactive comment on “Retrieval of O₂(¹Σ) and O₂(¹Δ) volume emission rates in the mesosphere and lower thermosphere using SCIAMACHY MLT limb scans” by Amirmahdi Zarboo et al.

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We would like to thank the referee for the careful review of the paper.

p.2 (1-3) and Figure 1 The recombination of atomic oxygen, reaction (R1) of the manuscript, is one of the primary reactions in the production of the emissions stud-

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ied in the manuscript. The authors list the likely product states of R1: ⁵Π_g and the Herzberg states c¹Σ_u⁻, A³Δ_u, and A³Σ_u⁺, but then add “has been a matter of dispute for some years”, without identifying what is disputed. The statement is then made: “The c¹Σ_u⁻ state is considered the most probable (Slanger and Copeland, 2003).”

Response: In our response we take into account the comments from both of the reviewers. The following has been added to the manuscript:

O₂^{*} represents any of the seven states below the first dissociation limit. Bates and others argue that the population distribution between these states can best be approximated statistically, in which the ⁵Π_g state is produced in almost 40% of the collisions (Smith, 1984; Bates, 1992; Wraight, 1982). Most of the O₂^{*} derived from recombination is found in the A³Σ_u⁺ state (Slanger and Copeland, 2003), and in a recent review Huestis concludes that all of the recombining atoms pass through the Herzberg states c¹Σ_u⁻, A³Δ_u, and A³Σ_u⁺ (Huestis, 2013). Stegman and Murtagh (1991) provide the quenching parameters resulted from analysing the measurements of the near-ultraviolet portion of the nightglow to fit the synthetic spectra of the Herzberg bands of O₂. These parameters set an upper limit of 10% production efficiency on the generation of O₂(c¹Σ_u⁻) in the atomic oxygen association reaction. Admittedly, proper accounting of the correct products of (R1) can be complex. Recent research has investigated this issue, e.g. Kirillov (2012, 2014). Therefore we assume the production of a surrogate “hybrid” state O₂^{*} in the photochemical model.

p.3(19),p.3(24),p.3(22),p.4(8): “spin-conserved” and “spin-forbidden”. The spin of the reactants and products is clearly defined in the associated equations and, indeed, most of the relevant transitions in both atomic and molecular oxygen are “spin-forbidden”. It might be better for the authors to also guide the reader towards the conclusion they intend to convey: Is the particular reaction exceptionally fast? Is the particular reaction

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exceptionally slow or negligible?

Done. The corresponding parts of the manuscript were modified.

p.5(6) Recommend changing "... (0,0), (0,1), and (1,1) vibrational band emissions ..." to "...O₂(¹Σ) (0,0), (0,1), and (1,1) vibrational band emissions...". The way the paragraph begins on p.4(25) makes it unclear that only O₂(¹Σ) is being discussed.

Changed as suggested.

p.5(22-23) A new section heading: "1.2 Present Work" is needed.

Done. A new section heading is added.

p.6(11-12) "...we use ... channel 4 ... and ... channel 6 ...". Using these two channels allows monitoring the 0–0 bands of O₂(¹Σ) and O₂(¹Δ), but why not yet more? SCIAMACHY has eight channels covering uv to the far ir. Could additional channels also have been used to monitor other oxygen emissions such as the green line or uv emissions from the Hertzberg states? It would be useful to state the limitations or possibilities of the SCIAMACHY data set.

Response: Use of the additional channels covering the green line or UV is beyond our current work, and we refer to e.g. Lednyts'kyi et al. (2015).

Change in the manuscript:

"In this work, we use the visible and near infrared spectra from channel 4 (595–811 nm)

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and channel 6 (1200–1360 nm) in the MLT limb viewing geometry to retrieve volume emission rates (VERs) from the airglow of the O₂(¹Σ) and O₂(¹Δ) bands. Use of the additional channels covering the green line or UV is beyond our current work, and we refer to e.g. Lednyts'kyi et al. (2015). "

p.6(16-17) "We subtract the spectrum measured at ~ 360 km tangent height as a dark spectrum from the measured spectra at all of the other tangent heights." This is likely appropriate, but the reader is not shown the 360 km spectrum. Is it intense? Does it have features? A bit of description regarding this dark spectrum would be helpful.

Response: This spectrum contains some residual (read-out) patterns left from the calibration step and subtracting it from other spectra which have the same patterns cancels out that.

Change in the manuscript: " We subtract the spectrum measured at ≈ 360 km tangent height as a dark spectrum from the measured spectra at all of the other tangent heights. This spectrum contains some residual spectral (read-out) patterns left from the calibration step and subtracting it from other spectra which have almost the same patterns cancels out that."

p.8 Figure 3a and 3c. These two figures show the twilight O₂(¹Σ) radiance without- and with-background subtraction. Yet to this reviewer, these figures appear identical. If the background is truly negligible, it would be helpful to confirm that in the text at p.8(3).

Response: The following is added to the manuscript:

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“It is apparent that the background signal is negligible for both of the $O_2(^1\Sigma)$ and $O_2(^1\Delta)$ twilight spectra.”

p.16(3) "...suspect that these abrupt changes are related to a change in the altitude sequence of the satellite measurements..." This seems very important!. Should not the effect of the altitude sequence on measured intensities be discussed a bit- perhaps in Section 2 of the manuscript? Should the data set presented in this manuscript be truncated at November 2010?

Response: In our response we take into account the comments from both of the reviewers. The text now reads as follows:

“Figures 8c, 8d, and 8f, show a decrease in the altitude of the maximum $O_2(^1\Sigma)$, altitude of the maximum $O_2(^1\Delta)$, and $O_2(^1\Delta)$ h_{CA} , respectively between November 2010 and February 2011. This is due to a change in the limb sequence

p.17(1) Are the rates A1, A3, A4 given in the "JPL Recommendation"? If not, where are they coming from?

Accepted. We used Einstein coefficients for the following transitions:

Change in the manuscript: “Einstein coefficients for the $O_2(^1\Sigma) \rightarrow O_2(X^3\Sigma_g^-)$ transition (A_2 in Figure 1) were taken from Mlynczak and Solomon (1993), for the $O(^1S) \rightarrow O(^1D)$ transition (A_4 in Figure 1) was taken from NIST atomic spectra database ¹, for the $O(^1S) \rightarrow O(^3P)$ transition (A_5 in Figure 1) was taken from NIST atomic spectra database, and for the O_2^* products (not given in Figure 1) were taken from Stegman and Murtagh (1991).”

¹www.nist.gov

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p.17(2) Is the "...quenching of the intermediate $O_2c^1\Sigma_u^-$..." the q6 and q7 rates shown in Figure 1, but not otherwise mentioned in the manuscript?

Accepted; Yes, that are the rates q6 and q7 given in Figure 1. Included a note about this in the text.

Change in the manuscript: “Reaction rates were taken from the JPL recommendation (Burkholder et al., 2015) with the exception of the quenching of the intermediate $O_2(c^1\Sigma_u^-)$ state (the q6 and q7 rates shown in Figure 1), which was taken from (Stegman and Murtagh, 1991) with δ coefficients from (Bates, 1988).”

p.19(7) Insert a comma (",") between "below 90 km" and "by photolysis of ozone".

Done.

References

- Bates, D.: Excitation and quenching of the oxygen bands in the nightglow, Planetary and space science, 36, 875–881, 1988.
- Bates, D.: Nightglow emissions from oxygen in the lower thermosphere, Planetary and Space Science, 40, 211 – 221, doi:10.1016/0032-0633(92)90059-W, 1992.
- Burkholder, J., Sander, S., Abbatt, J., Barker, J., Huie, R., Kolb, C., Kurylo, M., Orkin, V., Wilmouth, D., and Wine, P.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies–Evaluation Number 18, Nasa panel for data evaluation technical report, 2015.

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- Huestis, D. L.: Current Laboratory Experiments for Planetary Aeronomy, pp. 245–258, American Geophysical Union, doi:10.1029/130GM16, 2013.
- Kirillov, A.: The calculation of quenching rate coefficients of O₂ Herzberg states in collisions with CO₂, CO, N₂, O₂ molecules, *Chemical Physics Letters*, 592, 103 – 108, doi:10.1016/j.cplett.2013.12.009, 2014.
- Kirillov, A. S.: Model of vibrational level populations of Herzberg states of oxygen molecules at heights of the lower thermosphere and mesosphere, *Geomagnetism and Aeronomy*, 52, 242–247, doi:10.1134/S0016793212020077, 2012.
- Lednyts'kyy, O., Von Savigny, C., Eichmann, K. U., and Mlynczak, M. G.: Atomic oxygen retrievals in the MLT region from SCIAMACHY nightglow limb measurements, *Atmospheric Measurement Techniques*, 8, 1021–1041, doi:10.5194/amt-8-1021-2015, 2015.
- Mlynczak, M. G. and Solomon, S.: A detailed evaluation of the heating efficiency in the middle atmosphere, *Journal of Geophysical Research: Atmospheres*, 98, 10 517–10 541, 1993.
- Slanger, T. G. and Copeland, R. A.: Energetic Oxygen in the Upper Atmosphere and the Laboratory, *Chemical Reviews*, 103, 4731–4765, doi:10.1021/cr0205311, 2003.
- Smith, I. W. M.: The role of electronically excited states in recombination reactions, *International Journal of Chemical Kinetics*, 16, 423–443, doi:10.1002/kin.550160411, 1984.
- Stegman, J. and Murtagh, D.: The molecular oxygen band systems in the UV nightglow: measured and modelled, *Planetary and Space Science*, 39, 595–609, 1991.
- Wraight, P.: Association of atomic oxygen and airglow excitation mechanisms, *Planetary and Space Science*, 30, 251 – 259, doi:10.1016/0032-0633(82)90003-4, 1982.