

In the present manuscript, Zarboo et al. make an important contribution in presenting the volume emission rates of two molecular oxygen species as a function of altitude and season from limb-scans of the Earth's dayglow observed by the SCIAMACHY instrument on the ESA Envisat satellite. These data are particularly important in that the emissions of the two species,  $O_2(^1\Sigma)$  and  $O_2(^1\Delta)$ , are measured simultaneously, allowing their variations to be correlated with photochemical processes in MLT region of the terrestrial atmosphere. The authors develop a photochemical model for the atmospheric reactions involving  $O_2(^1\Sigma)$  and  $O_2(^1\Delta)$ , use this model to draw conclusions from the emission measurements, and point to its potential use in monitoring ozone.

The present manuscript certainly has the potential for publication. There is, however, one area of the manuscript that clearly requires correction, and several others, enumerated below by page and (line number(s)), that would benefit from revision.

**The portion of the manuscript requiring correction is:**

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 studied in the manuscript. The authors list the likely product states of R1:  $^5\Pi_g$  and the Herzberg states  $c\ ^1\Sigma_u^-$ ,  $A'\ ^3\Delta_u$ , and  $A\ ^3\Sigma_u^+$ , but then add "has been a matter of dispute for some years", without identifying what is disputed. The statement is then made: "The  $c\ ^1\Sigma_u^-$  state is considered the most probable (Slanger and Copeland, 2003)."

What the referenced Slanger and Copeland review actually says regarding Reaction R1 (their Eqn. 2):

" $O_2^*$  represents any of the seven states lying below the first dissociation limit, and it has been argued by Bates and others that the population distribution between these states can best be estimated statistically, in which case the  $^5\Pi_g$  state should be generated in about 40% of all collisions." Continuing in their Section 16 they state: " It is now evident that much of the  $O_2$  production derived from recombination is to be found in the  $A\ ^3\Sigma_u^+$  state; in a recent review it was concluded that 100% of the recombining atoms go through the Herzberg states." Finally, the source of the authors' quenching rate constants (Stegman and Murtagh, 1991) "...set an upper limit of 10% on the production efficiency of  $O_2\ c\ ^1\Sigma_u^-$  ...".

Consequently, this reviewer finds little support for the authors' choice of the  $c\ ^1\Sigma_u^-$  state as the sole molecular product of R1. Radiation from each of the Herzberg states is observed in the terrestrial nightglow (see Cosby et al., *J. Geophys. Res.*, 111, A12307, doi:10.1029/2006JA012023 and references therein) into *vibrationally excited* levels of the  $X\ ^3\Sigma_g^-$ ,  $a\ ^1\Delta_g$ , and  $b\ ^1\Sigma_g^+$  states. Collisional quenching of the Herzberg states yields *both* a  $^1\Delta_g$  and  $b\ ^1\Sigma_g^+$  state products (Slanger and Copeland, 2003).

Admittedly, proper accounting for the products on R1 can be complex. There is active research towards understanding this, e.g. A. S. Kirillov, *Geomagnetism and Aeronomy*, 2012, Vol. 52, No. 2, pp. 242–247; *Chem. Phys. Letters* 592, 103-106 (2014). Perhaps use of a surrogate state in the photochemical model will be appropriate. However the authors should clearly delineate whatever approximations are being made.

**The following areas of the manuscript would benefit from revision:**

p. 3(19), p3(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 exceptionally slow or negligible?

p. 5(6) Recommend changing "... (0,0), (0,1), and (1,1) vibrational band emissions..." to "...  $O_2(^1\Sigma)$  (0,0), (0,1), and (1,1) vibrational band emissions...". The way the paragraph begins on p. 4(25) makes it unclear that only  $O_2(^1\Sigma)$  is being discussed.

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

p. 6(11-12) "... we use ... channel 4 ... and ... channel 6 ...". Using these two channels allows monitoring the 0-0 bands of  $O_2(^1\Sigma)$  and  $O_2(^1\Delta)$ , 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 Herzberg states? It would be useful to state the limitations or possibilities of the SCIAMACHY data set.

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.

p. 8 Figure 3a and 3c. These two figures show the twilight  $O_2(^1\Sigma)$  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).

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?

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

p. 17(2) Is the "...quenching of the intermediate  $O_2$  c  $^1\Sigma_u^-$  state..." the  $q_6$  and  $q_7$  rates shown in Figure 1, but not otherwise mentioned in the manuscript?

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