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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 #3

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The paper "Atmospheric band fitting coefficients derived from self-consistent rocket-borne experiment" by Grygalashvyly et al uses observations of temperature, total air density, atomic oxygen and the $O_2(^1\Sigma)$ volume emission rate from a night-time rocket experiment of March 2015 to derive fitting coefficients for the formation of the emission signal considering three different formation pathways: direct formation, formation via an intermediate excited state, and a combination of both. The first two formation pathways are a repetition of a similar experiment from the ETON campaign as discussed in McDade et al 1976, which however had to use model values for temperature and total air density; the combination pathway is a new development as far as I know, though results suggest that the formation via an intermediate state dominates. This is an inter-

esting study, and considering that such fitting coefficients are used to derive night-time atomic oxygen density from observed volume emission rates of the O2 atmospheric band, highly relevant. However, I found that the paper clearly needs more work before final publication. My main concerns, listed below in more detail, concern the error analysis - errors are provided in some of the figures, but it is not explained how they are derived, and no error range is given for the end results of the analysis, the coefficients and efficiencies. This has to be provided in the final publication. Also, the derived coefficients are not compared directly to the results of the previous study by McDade et al; I found this really curious, as they are actually very different in particular concerning the coefficient of O-quenching, C^O. This really must be discussed. Can this large difference really be due to different temperature profiles used? And finally, the description of the data used, in particular of the volume emission rates, lacks important information needed to understand/interpret the results. In summary, I recommend publication only after major revisions, see list below.

Major comments:

Lines 107-111: considering that the volume emission rates are crucial for deriving the fitting coefficients for the $O(^3P)$-model, this explanation about how they are derived is totally inadequate. I appreciate that this might be explained in detail in Hedin et al. (2009), but information needed to interprete the results must be given here as well. These include: a) the viewing geometry of the instrument. Is it looking in flight direction of the rocket (in which case it would see roughly the same volume of air as the in-situ instruments at least when far away from the rockets apogee), or is it looking to the side (in which case it would not see the same volume of air as the in-situ instruments)? How are volume emission rates derived, and how large is the volume viewed by the instrument? How far away is it from the rocket path viewed by the in-situ instruments? What about the spectral resolution / coverage of the instrument? What's the measurement uncertainty, and why? What is the vertical resolution? Presumably a few km, why? And how will that affect a comparison with in-situ observations which have a much better resolution?

Section 3: Throughout reading of section 3, I have wondered why you are not discussing a combined one-step/two-step mechanism. Turns out much later that you do, but the theory for that is discussed only in the Appendix. Why? As the combined mechanism seems more likely, and also seems to be a new development here, I would do it the other way round - discuss the combination here, and the individual mechanism in the Appendix. However, that is your decision (and I appreciate that you do not discuss all three here as that would be rather long). However, no matter whether you discuss the individual steps or the combined in section 3, you should really point out already in section three that you test all three posibilities (one-step, two-step, combined) in the paper, and that the derivation of the coefficients of the branches not discussed here is discussed in the Appendix.

Line 131-132: please also state that you have to assume photochemical equilibrium of $O_2(^1\Sigma)$ to derive equation (1).

Line 144: please also state that you have to assume photochemical equilibrium of O2* to derive equation (4).

Same in line 149: you have to assume photochemical equilibrium of $O_2(^1\Sigma)$. How valid is this assumption?

Lines 156-157: As you derive the coefficients C^O and C^{O2} over the whole altitude range, you have to assume that the coefficients are temperature independent. This means that the reaction rates k_3 are either temperature independent, or have the same temperature dependency for all quenching partners (N2, O2, O), correct? Is this a valid assumption?

Lines 194-196, Figure 2: What is the meaning of the error bars in Figure 2? How/from which uncertainties have they been derived? Considering the very large errors given

here, I would assume that this is not the measurement noise, as the error bars are actually much larger than the scatter of the measurement points.

Line 197: considering the error range of the individual altitudes, the range is rather 0.03-1.17. However, there is a common range including all data points and their errors which is much narrower, more like 0.07-0.10. However, you really should provide the most likely result based on the measurement statistics here, i.e., the mean or medium point plus/minus the standard error taking into account both the variance and the error range of the individual points.

Line 198: please provide the mean/median with error range based on the variance and error range of the individual points.

Line 199-200: considering the large error range, there is no significant altitude dependence. You can of course discuss it anyway, but please keep in mind (and state in the paper) that the variability of the data points is much smaller than the errors of the individual points.

Line 203: "values are distributed not randomly" ...well the altitude spacing shown in Figure 2 is obviously much smaller than the vertical resolution of the volume emission rates they are based on, compare to Figure 1 d), so I would expect of course there a non-random underlying altitude dependence - it comes from interpolation (or splining, or whatever) of the volume emission rate between data-points. Please discuss in the paper a) how volume emission rates are derived between data-points (interpolation, spline?), and b) how this affects the results.

Line 203: "clear functional dependence ..." well I see at least three functional dependencies here. I agree with your discussion below (lines 205-208) that one would expect a dependence on temperature and pressure due to the T/p dependence of the reaction rates; however, I think considering your large errors, and the fact that the low vertical resolution of the volume emission rates must imply an auto-correlation between data-points (see comments above), you can't really derive any evidence for this from your data.

Line 235: values of C^{O2} and C^{O}: please provide an error range based on error propagation from the error and variance of RHS as provided in Figure 4. Also, please compare these values directly with the values given by McDade et al 1976. Do they agree within the error range? The values are: your data: $[C^{O2}; C^{O}] = [9.8; 2.1]$; McDade: $[C^{O2}; C^{O}] = [4.8 - 7.5; 15 - 33]$. My expectation would be that they do not agree within your error range, particularly not C^{O} which really is very different. Please discuss. Also, what could be the reason for the large discrepancy in C^{O}? Temperature dependence of the O-quenching? Or the use of the atomic oxygen profile? Please discuss.

Line 238: please discuss how well-funded the assumption is that quenching with N2 is much slower than quenching with O2. Is there any evidence for that?

Line 238: please provide error range for alpha gamma.

Line 250: please provide a symbol for the total efficiency, and use this symbol in the equation. tot.eff really looks unprofessional in the equation.

Line 257: please consider the error of alpha and the total efficiency 0.102 here. However, I would not expect this to change the conclusions here. Same in line 310.

Line 268: please provide error range

Lines 283 ff discussion of Fig 5: considering that you used the FIPEX data to constraints your coefficients, the agreement is not that good, actually; in particular, the shape of the profile appears slightly different, with the peak maximum at a higher altitude than the observation. In this, your result resemble the McDade results; maybe because in both cases, the ratio of two reaction rates is derived, not the rates themselves? In the lower part your results and those of McDade differ, presumably because C^{O} is so different? Please discuss this difference from the comparison of the coefficients.

Line 316 ff discussion of Figure 7: Considering the volume emission rate observation you use here for comparison is the same that you used to constraint the coefficients of your model, this is more a sanity check than a validation. For a validation, you would have to compare your results to an independent measurement.

Line 349: please provide error range of results. Please make a statement about how those values compare to previous derivations (McDade 1976).

Lines 358, 359: please provide error range of results.

Minor comments:

Line 32-33: This sentence is too short; it's meaning is not clear at all. Please clarify: Why is the mesopause important for the upper atmosphere (which presumably is above the mesosphere?) Coupling between which atmospheric layers is important here? Presumably between mesosphere and thermosphere?

Line 40: "the tides parameters" is either "the tidal parameters" or "the tides' parameters"

Line 43: However, Takahashi et al used the (0,1) transition of the atmospheric band at 864,5 nm, while you use the (0,0) transition at 762 nm. The (0,0) transition was used however by Sheese et al CJP 2010, GRL 2011, and this should be discussed here.

Lines 54-55: please make clear that you are talking about the night-time population here; during day-time, the excitation mechanism of the atmospheric band are quite different, being dominated by $O(^1D)$ quenching and resonance fluorescence (see, e.g., Zarboo et al, AMT, 2018, Figure 9).

Lines 61-62: "the" hypothesis, "the" precursor

Lines 64-65: problem of identification is still not solved; the breakthrough ... this seems to be a contradiction. in particular considering that the ETON results were published in

1976 so are not recent at all. I agree that despite the ETON results there are still many open questions, but this should be formulated more carefully (and more clearly) here.

Line 126: "saving all nomenclature..." you mean "using all nomenclature..."?

Line 133: "fraction of recombination" this is actually the fraction of the three-body recombination reaction that directly leads to $O_2(^1\Sigma)$. I found the term "fraction of recombination" misleading here (same in line 140); I would probably call this the "quantum yield of $O_2(^1\Sigma)$ formation".

Line 142-143: R8 is one pathway of the overall quenching reaction R9; this should be made clear here.

Line 227: "too low" really should be "much lower".

Line 233: It would help the reader to write "right hand side (RHS) of equation ..." once again here.

Line 233: "are amount to" $\longrightarrow$ "amount to"

Line 235: "in such a way define fitting-coefficient" $\longrightarrow$ "fitting-coefficients defined in such a way ..."

Line 320: erase one "the" before temperature.

Line 359: what does "a sense of" mean here?

Line 365: please erase "to" after "contradict"

Line 366: please insert "is" after "mechanism"

Figure 7: the figure is hard to read - lines are too thin, and the resolution appears to be low.

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