Interactive comment on “Technical Note: A new mechanism of 15 µm emission in the mesosphere-lower thermosphere (MLT)” by R. D. Sharma

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1 General comments

The manuscript deals with a dominant cooling mechanism in the MLT of Earth which is also important for other CO₂-containing planetary atmospheres (i.e. Martian and Venusian). It is well known that both the calculated radiative cooling/heating and calculated 15 µm radiance strongly depend on the rate coefficient for \( CO_2(\nu_2) + O \) collision, \( k_{VT} \). At the same time, there is a known discrepancy between laboratory measurements and atmospheric estimates of the \( k_{VT} \). The manuscript attempts to close this knowledge gap and, therefore, is definitely worth discussing in the ACPD: even if the proposed explanation for the lab-atmosphere discrepancy might be not the ultimate one (I will try to prove my point below), drawing the readers’ interest to the problem is important since this can stimulate other studies in this field.

The author suggests a new mechanism of energy exchange between \( CO_2(\nu_2) \) vibrational levels and a thermal reservoir. The reasoning is clear and the estimates for the \( CO_2(\nu_2) \rightarrow N_2 \) exchange rate coefficient are of a right order of magnitude (see the specific comments for the discussion of the values), but the only major objection I have is that the proposed mechanism only partially explains existing discrepancies. In reality, the situation with the \( k_{VT} \) is even worse than it was discussed in the papers mentioned in the manuscript. At the moment, one should consider three values of rate coefficient: 1) \( k_{LAB} \) measured in the laboratory; 2) \( k_{ATM} \) retrieved from atmospheric observations; and 3) \( k_{GCM} \) used in the circulation models. Roughly, \( k_{LAB} = \frac{1}{2} \times 10^{-12} \text{cm}^3\text{s}^{-1} \), \( k_{ATM} = 6.0 \times 10^{-12} \text{cm}^3\text{s}^{-1} \), and \( k_{GCM} = 3.0 \times 10^{-12} \text{cm}^3\text{s}^{-1} \). The \( k_{GCM} \) has been selected as a 'median' value for the GCMs of Earth, Mars, and Venus, and comparisons with satellite observations do not justify using \( k_{ATM} \). This is an indirect proof that the discrepancy in the \( k_{VT} \) values should not be associated with the processes linked to thermal reservoir. I agree with the vulnerability of "hot oxygen" concept proposed in [Feofilov et al., 2012], but this concept makes \( k_{LAB} \), \( k_{ATM} \), and \( k_{GCM} \) consistent with the current knowledge: a) "hot" oxygen (or similar but unknown component) gives extra pumping to \( CO_2(\nu_2) \) levels making it necessary to use an "effective" \( k_{ATM} \) for an adequate interpretation of temperature retrievals from the 15 µm emissions; b) "hot" oxygen is deliberately eliminated in laboratory experiments, leading to \( k_{LAB} \); c) no extra energy transfer from thermal reservoir is necessary in model calculations, so one can use \( k_{LAB} \) or currently accepted \( k_{ATM} \) to estimate cooling/heating rates in the GCMs. If hot oxygen energy really dissipates before reaching \( CO_2(\nu_2) \), pumping mechanism still should be similar to that proposed by [Feofilov et al. 2012] in a sense that no extra energy transfer from
thermal reservoir should exist.

I have made non-LTE calculations with the MLS atmospheric model described in details in [Feofilov and Kutepov, 2012]. Three curves in Fig. 1a correspond to three values of \( k_{VT} \). Two curves in Fig. 1b correspond to changes in broadband 15 \( \mu m \) emission calculated for channel #3 of the SABER radiometer with respect to radiance calculated with \( k_{LAB} \). As one can see, for the MLS conditions, which are close to that over Fort Collins the sensitivity to \( k_{VT} \) is high above 85–90 km altitude. Current knowledge is that the mechanism of 15 \( \mu m \) radiance formation should correspond to red curve \( (k_{GCM}) \) in Fig. 1a AND to blue curve \( (k_{ATM}) \) in Fig. 1b. Adding the mechanism proposed in the manuscript to the non-LTE model of CO\(_2\) will lead to blue curve \( k_{ATM} \) in both panels that will over-cool the MLT area in the GCMs.

Summarizing, I recommend publishing this paper in ACP after the discussion of using \( k_{VT} \) in the circulation models is added, the aforementioned discrepancies are addressed, and test atmospheric model is described or referenced. The specific comments below should also be addressed.

2 Specific comments

Line 1: Since the proposed mechanism is still hypothetic, I would change the title of the manuscript to "On the possibly missing mechanism of 15 \( \mu m \) emission in the mesosphere-lower thermosphere (MLT)" or to something of this kind.

Line 30: it is just a question of definitions, but I would not start with process (1) written in this way. A two-step notation:

\[
CO_2(0^000) + O(3P) \rightarrow CO_2(0^110) + O(3P);
\]

\[
CO_2(0^110) \rightarrow CO_2(0^000) + h\nu (667\text{cm}^{-1})
\]

would look stricter.

Lines 51–53 and below: it is not clear, which atmospheric model was used by the author. Temperature of 272 K at 105 km altitude corresponds to subarctic summer, SAS (i.e. see Fig. 5 in [Feofilov and Kutepov, 2012]) while the discussed comparison with Fort Collins is closer to the MLS conditions where the temperature at 105 km height is \( \approx 230 \) K. This will affect numerical estimates in lines 117–122.

Line 52: may be, it makes sense to rename \( k_u \) to \( k_X \) to exclude any associations with \( k_{UP} \) (a reverse to \( k_{DOWN} \) in kinetics)? Letter "x" traditionally corresponds to "unknown" and "uneXplained".

Lines 64–66: indeed, the collisions with other atmospheric molecules are much more frequent than that with CO\(_2\). However, the process of energy transfer is non-linear and, roughly speaking, the higher the speed the less time for energy exchange the system has, so I would not exclude this channel completely. Another option is to use an abundant mediator molecule for an explanation of pumping from hot oxygen. Without this channel, the aforementioned problem of using high \( k_{VT} \) value in the circulation models will remain.

Lines 68–70: pumping mechanism described in these lines is not similar to energy exchange with rotational-translational energy reservoir. This is again related to the problem mentioned at the end of General Comments section. Indeed, one needs an explanation like ‘chemical pumping’ or ‘photochemical pumping’, but the proposed mechanism of energy transfer from rotational levels of N\(_2\) does not belong to this class.
Lines 117–120: as discussed before, the value of 272 K seems to be an overestimate. Correspondingly, the populations of 4 levels of \( N_2 \) are overestimated. One should either describe an atmospheric model or justify using these values. It would be better to provide a vertical profile of \( k_u \) (or \( k_X \)). I have estimated the ratio of \( N_2(J=15-18) \) population to volume mixing ratio of \( O(3P) \) and found it to be almost constant above 90 km and equal to \( \approx 0.5 \). This immediately gives an estimate of \( k_u \) and proves that the hypothesis of energy transfer from \( N_2 \) is technically correct (see above for the concerns regarding scientific justification of accepting this hypothesis). This can be used in the discussion.

3 Technical corrections

Line 92: please, change "large" to "larger"

Line 191: please, change "Gusov" to "Gusev"

4 References


Full figure caption:
Fig. 1. Sensitivity of calculated profiles to \( k_{VT} \) estimated for the MLS type of atmospheric profile: a) cooling/ heating rate for three values of \( k_{VT} \), b) broadband 15 \( \mu \)m radiance calculated for two values of \( k_{VT} \) and compared to radiance profile calculated with \( k_{LAB} \).

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Fig. 1. Sensitivity of calculated profiles to KVT.