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Atmospheric Chemistry and Physics Discussions

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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General comments:

This work address a very old and important aspect (still unsolved) of the upper atmospheres of the terrestrial planets affecting their temperature structures. It is also important nowadays for the remote sensing of the temperature of the Earth's upper atmosphere as it has become feasible to measure the CO2 15 μm limb emission of this tenuous atmospheric region and we are limited by the mechanisms and uncertainties of the (de-)excitation of CO2(010) by atomic oxygen and other possible atmospheric species.

It is generally accepted by the community differences in the values of that coefficient measured in the laboratory and derived from atmospheric measurements (although the magnitude of those differences are unclear because of the large (and sometimes not described or underestimated) errors of the coefficient derived from atmospheric measurements. Therefore, a possible mechanism that can help for understanding that discrepancy is most welcome. The proposed mechanism seems, in principle, plausible, but its rate coefficient should be measured in the laboratory first, in order to make a realistic quantitative estimation of its impact. Also, I have some doubts about the value of the RV rate coefficient for CO2-N2 collisions derived in the manuscript for explaining the laboratory/atmospheric discrepancy. First, because the author uses a single case of the values for temperature and atomic oxygen at 90 and 105 km, when we know that those quantities have a large atmospheric variability. Secondly, because they assumed a single case of the derivation of the laboratory/atmospheric discrepancy, based on the values of K(CO2-O) derived by Feofilov et al. (2012), which I think has larger errors than those stated in that reference. Furthermore, unless I have incurred in a significant error, my calculations show, based on realistic SABER measurements, that the required value should be significantly larger. In addition, if such mechanism would be at work, it might have other important implications, e.g. for the non-LTE populations of the CO2(0v20), with v2=2,3, and of the isotopic CO2(010) levels around the mesopause. With the additional mechanism they might be more thermalized, with possible implications on the retrieved temperature from CO2 15 μm emission, as, e.g.. SABER.

Thus, although the idea is very interesting, I am not fully convinced that this mechanism is operating in the atmosphere. From my point of view it still requires some calculations, as those shown here, and certainly a laboratory measurement. The later would give us the motivation for considering its potential impact on the global CO2 non-LTE emissions. I do not want, however, to prevent the author from publishing this idea. If so, however, I would strongly recommend to include my comments below.

It is also clear that as it is an hypothesis which should be reflected in the title, e.g., "a

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"potential" or "possible" new mechanism".

Specific comments:

I do not fully agree on the quantification of the "unaccounted" rate coefficient, e.g., difference between the laboratory measurements and the derivation from atmospheric measurements. The derivation of the atmospheric value has a very large uncertainty, as much as 50\% (or 100\%). That is it can be 3e-12 (see below) instead of 6e-12 (Sharma and Wintersteiner, 1990) or 8e-12 (Feofilov et al., 2012). The reason is that, to derive the rate from CO2 15 μm limb emission measurements, one have to measure simultaneously, the pressure, temperature, CO2 abundance and atomic oxygen abundance. None of those parameters were measured in the dataset used for the derivation of that rate in some of the references mentioned by the author (e.g., Sharma and Wintersteiner, 1990; Stair et al., 1985; Sharma, 1987). Secondly, the rates derived by Feofilov et al. (2012) are based on the atomic oxygen measured by SABER. It has be found recently that this might be overestimated by a factor of 2 (Kaufmann et al., 2014). Also, SABER does not measure O above around 95 km (Mlynczak et al., 2013), hence the value derived by Feofilov et al (2012) at 105 km might be biased by as much as a factor of 2 (it is well known the large variability of O at these altitudes). Thirdly, the author did not included in the discussion the derivation of the rate based on ATMOS measurements (Lopez-Puertas et al., 1992). This is probably the most accurate value derived from atmospheric measurements since ATMOS observations provided, simultaneously, the pressure, kinetic temperature, CO2 abundance and CO2(010) Tv. The only quantity not measured was O; and they derived a value between 3e-12 and 6e-12 depending on the atomic oxygen. Definitely this derivation should be discussed in the manuscript.

The estimation of the required rate coefficient needed for the "unaccounted" rate in Sec. 3 is far from being representative of the atmospheric conditions, and the value the author derives (page 25089, line 5) of 4.1e-13 at 105 km is, according to my estimations, too small by about one order of magnitude. Fig. 1a shows for 29 June 2005

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(a typical day of solstice conditions) the profiles of the V-T deactivation of CO2(010) by N2 (process 1a in Table 5 of Funke et al. (2012)), e.g. K*N2, with N2 in ppv ($\sim$0.78) (included as reference); the de-activation of the proposed mechanism K(RV)*N2(j=15-18) (calculated for the measured temperature shown in Fig. 1c) for the estimated value of 4.1e-13 (Fig. 1a) and a value of 6e-12 (Fig. 1b); and the de-activation rate of VT with O with the assumed value of the author, 6e-12. The used temperatures and O abundances are shown in Figs. 1c and 1d. O and correspond to SABER observations. O was measured by SABER up to $\sim$90-95 km and merged with MSIS above.

Fig. 1a shows: a) The value of 4e-13 is clearly not sufficient to compete with the currently VT-O de-excitation process. It is needed at least a value of 6e-12 to make it comparable to the VT O mechanism (Fig. 2b); b) The statement in the conclusion (page 25089, lines 19-21) that "It is this rapid increase in temperature and not the rapid increase in atomic oxygen density that explains rapid increase in unaccounted rate coefficient." does not hold for almost all atmospheric conditions: most of the red lines in Figs. 1a and 1b are nearly constant (or even decreasing) with altitude up to about 105 km and with gradient much smaller than the KVT-O. Only for the few profiles around the polar summer region the new mechanism has a larger gradient than the VT-O. That is, this mechanism provide, in general, a much slower increase with altitude than the unaccounted rate coefficient; c) If the (de-)excitation of this new mechanism would be comparable to VT-O in the 105 km region, it would also induce a faster thermalization at 90-95 km. This might has an impact in the non-LTE populations of the CO2(v2=2-3) and CO2(010) isotopic levels, they would be more thermalized, which might have some impact on the retrieval of temperature from instruments measuring the CO2 15 μm emission in a broad band, as SABER.

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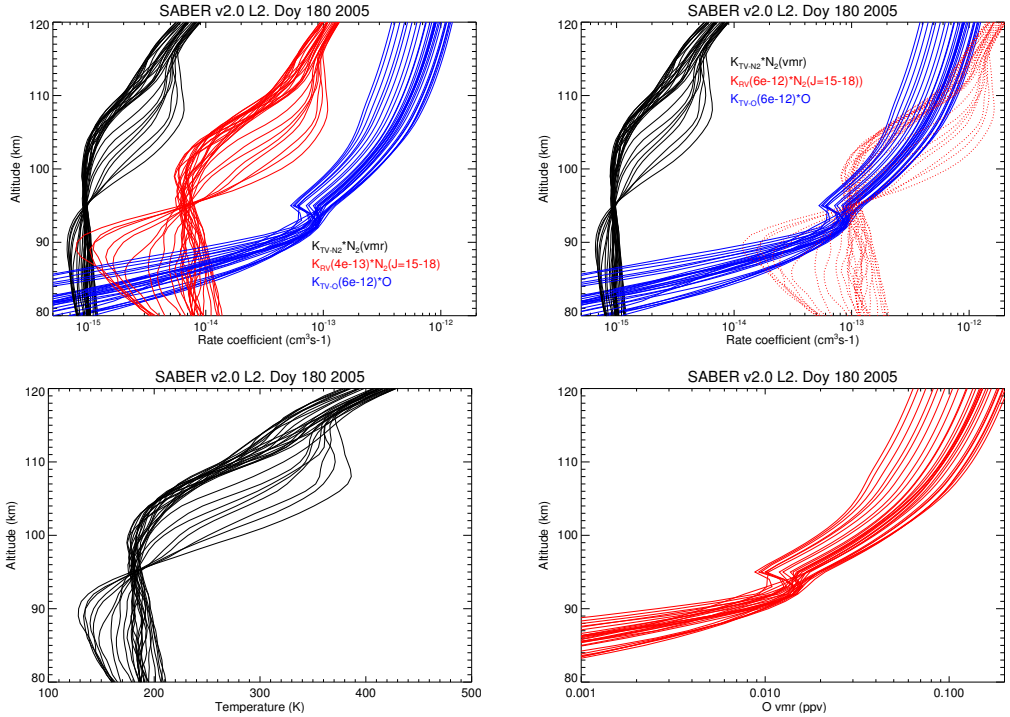

Fig. 1. Calculation of VT(CO2-N2), new proposed mechanism (RV CO2-N2), and VT (CO2-O) deactivation rates for one solstice day. Temperatures and O vmr are also plotted.

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