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Interactive comment on "$CO_2(\nu_2) - Oquenchingratecoefficientderivedfromcoincidental SABE$

Anonymous Referee #3

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The paper by Feofilov et al. presents a new results on the retrieval of the CO2-O quenching rate constant (kVT) from coincident SABER/TIMED and Fort Collins sodium lidar observations. Keeping in mind a crucial importance of kVT for estimation of the MLT (Mesosphere and Lower Thermosphere) energy balance, the paper can potentially provide a substantial contribution to our understanding of the MLT region and, hence, it can be published in Atmospheric Chemistry and Physics after some modifications described below.

I have a mixed feeling toward this paper. On one hand the topic of the paper and the results presented are quite interesting. On the other hand, there are some uncertainties about interpretation of the observations. Indeed, the best way to obtain a reaction rate constant is to measure this constant in laboratory conditions when all relevant processes are under control. The latter is unfortunately not the case for atmospheric retrievals. A few laboratory experiments carried out over the past two decades

showed a generally good agreement with a kVT value being around 1.5E-12 cm3/s. However, the values obtained from atmospheric retrievals are of about 4 times larger as indicated in Table 1 of the paper. This most likely tells us that some unknown processes are going on in a real atmosphere and these processes are not considered in NLTE models used for retrievals. The authors suggested that the discrepancy between laboratory measurements and atmospheric retrievals can be due the presence of hot (non-thermal) O and O(1D). This looks like a valid idea. However, there can likely be some other mechanisms for vibrational excitation of CO2 molecule, so these mechanisms should be, at least briefly, discussed. These mechanisms can include: (a) temperature dependence of kVT; (b) collisions with such species as H and OH (both thermal and non-thermal); (c) collisions with excited species O(1S), OH(v), etc (also both thermal and non-thermal); (d) collisions with charged components; and so on. Also, a possibility of multi-quantum excitation exists for collisions with thermal atomic oxygen as indicated in Ogibalov et al. (1998) and Ogibalov (2000).

I suggest to slightly refocus the paper by more strongly emphasizing the discrepancy in kVT obtained in laboratory measurements and in atmospheric retrievals. This discrepancy should be clearly mentioned in abstract and, preferably, in the title. All possible mechanisms of excitation, not only collisions with hot atomic oxygen, should also be discussed in the paper. And finally, the rate coefficient kVT retrieved in this work can be recommended as a provisional coefficient which, in the absence of clear understanding of all the excitational mechanisms, provides an efficient excitation attributed to CO2-O collisions only.

In addition, some clarification is required on how atomic oxygen and CO2 profiles used for this work were obtained. It is said in the paper that both these constituents were retrieved from the SABER/TIMED measurements. However, the CO2 retrieval is not published in any peer reviewed journals, but in a PhD thesis. So it would be very helpful for the readers if a few sentences describing the method, its accuracy and agreement with other measurements (e.g., CRISTA and ACE) are added. As for the atomic oxygen, the reference given by the authors (Mlynczak et al., 2007) describes derivation of atomic oxygen from DAYTIME mesospheric 1.27 micron emission. Whereas most of the profiles selected for the kVT retrieval fall in 18-6h local time interval (i.e., nighttime, see p.32586, l. 18). So, some clarification is needed here.

2. SPECIFIC COMMENTS

p. 32585, l. 16: Should it be "... values, obtained in laboratory AND retrieved by fitting..."?

p. 32587, l. 3-4: As seen from Table 1, atmospheric retrievals reported by Kumer and James (1983) and by Sharma and Nadille (1981) also showed low kVT values. Did you mean the most recent experiments? If so, please clarify.

p. 32587, l. 7: "...an average midlatitude atmospheric profile...". Profile of what, temperature, CO2, atomic oxygen, something else? Please clarify.

Section 3.1: You only discuss the atomic oxygen effect, but how good is the CO2 abundance known? Please discuss how the uncertainty in CO2 can effect the result. Also, why T-dependence of kVT is neglected?

p. 32588, l. 27: This approach is valid only if I(15um) depends linearly on Y, right? If so, this approach is likely not good for the mesosphere.

p. 32589, l. 18: "...fall in 18-6h local time." However, if atomic oxygen was obtained from DAYTIME emission (as described in Mlynczak et al., 2007), your criteria delta(t) < 10 min is broken. Please clarify.

p. 32590, l. 22-26: Strange argument. If SABER atomic oxygen is proven to be overestimated, this fact should be taken into account. In any case, such a large discrepancy between SABER atomic oxygen and atomic oxygen from other sources indicates that the observational error for, at least, atomic oxygen is larger than that assumed in the kVT retrieval and so, the accuracy of the retrieved kVT is much less than that quoted in the paper. Please discuss this issue in more detail.

p. 32591, l. 13: "... usually assumed that..." How good is this assumption?

p. 32593, l. 6-7: "We show..." You didn't show, but suggest or speculate.

p. 32593, l. 12-15: This is not a practical recommendation. As long as new mechanisms for the CO2 vibrational excitation are not revealed and rate constant for these mechanisms are not found, this recommendation can not be used in general circulation models.

3. TECHNICAL CORRECTIONS

p. 32586, l. 18: "... (translational degrees of freedom of atmospheric constituents)..."

p. 32585, l. 17: "...see Table 1 and Sect. 2 below..."

p. 32590, l. 14: "...values shown in Fig. 2c..."

p. 32592: Should it be (1-alpha) in eq. (5) and in the first term of eq. 4?

REFERENCES

Ogibalov, V. P., A. A. Kutepov and G. M. Shved (1998): Non-local thermodynamic equilibrium in CO2 in the middle atmosphere. II. Populations in the v1v2 mode manifold states. J. Atmos. Solar-Terr. Phys., 60, 315-329.

Ogibalov, V. P. (2000): The CO2 non-LTE problem taking account of the multiquantum transitions on the v2-mode during CO2-O collisions. Phys. Chem. Earth (B), 25, 493-499.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 32583, 2011.