Atmos. Chem. Phys. Discuss., 11, C16439–C16445, 2012
www.atmos-chem-phys-discuss.net/11/C16439/2012/

Atmospheric
Chemistry
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Discussions

Interactive comment on “CO$_2(\nu_2) - Oquenchingratecoefficientderivedfromcoincidental SABER/TIMED and Fo$

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Received and published: 18 April 2012

We thank the Reviewer 3 for his/her analysis and comments on the paper. The responses to major and minor comments are given below. We marked the reviewer's and the author's comments by “**RC:**” and “**AC:**”, respectively.

General comments

RC: On the other hand, there are some un-certainties about interpretation of the observations . . . there can likely be some other mechanisms for vibrational excitation of CO$_2$ molecule, so these mechanisms should be, at least briefly, discussed. These mechanisms can include: (a) temperature dependence of k$_{VT}$;
AC: This is a good point. Please, see the response to the 5-th general comment of the Reviewer 2.

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RC: (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).
AC: We have added all these mechanisms to the discussion as other possible sources of $CO_2(\nu_2)$ excitation. In our opinion, the most important point is to split the "traditional" $CO_2(\nu_2)$+O collisional process to the collisions with thermal oxygen and some other process, which can be b)-d) or the collisions with non-thermal oxygen. We have also added a reference to Ogibalov (2000).

RC: I suggest to slightly refocus the paper by more strongly emphasizing the discrepancy in k_{VT} 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.
AC: Actually, the second phrase in the abstract is "However, there is a factor of 3–4 discrepancy between various measurements of the CO_2-O quenching rate coefficient, k_{VT}" so the reader knows from the very beginning that the paper deals with this problem. As for the mechanisms of excitation, we have added some generalization to the discussion. We still consider collisions with hot oxygen to be the most probable source of extra pumping but we do not exclude the other sources. To make one step further, quantum-mechanical calculations for the collisions with non-thermal atoms and molecules are required.

RC: And finally, the rate coefficient k_{VT} 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 CO_2-O collisions only.
AC: This is correct. We added the corresponding phrase to the conclusion.

RC: In addition, some clarification is required on how atomic oxygen and CO_2 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 CO_2 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.
AC: The author of the Ph.D. thesis, Dr. Ladislav Rezac has kindly provided us with the download link to his thesis, which was added to the reference list. We have also added the figure, which shows ACE-FTS, WACCM, and SABER CO_2 VMR profiles.

RC: 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 k_{VT} retrieval fall in 18-6h local time interval (i.e., nighttime, see p.32586, l. 18). So, some clarification is needed here.
AC: We agree with this point. Indeed, the techniques are different during day and night although both rely on the assumption that ozone is in photochemical equilibrium. An overview of atomic oxygen retrieval from the SABER measurements is given in (Smith et al., 2010). During day, atomic oxygen is determined directly from the ozone. At night, atomic oxygen is calculated from the Meinel bands airglow emission from vibrationally excited hydroxyl (OH). There are uncertainties in both the day and night retrievals due to uncertainties in some of the important input parameters. However, the excellent consistency between the day and night atomic oxygen lends confidence to the methods used. To avoid the confusion, we have removed the reference to (Mlynczak et al., 2007) since the next reference to (Smith et al., 2010), which is provided in the next line of the text, covers both the daytime and nighttime atomic oxygen retrievals.

Specific comments

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

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RC: 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 k$_{VT}$ values. Did you mean the most recent experiments? If so, please clarify.
AC: The correction has been made to the text ("…and the values required for an adequate interpreting of atmospheric measurements performed in recent 20 years are usually about 5.5x10$^{-12}cm^3$ s^{-1}")

RC: p. 32587, l. 7: "...an average midlatitude atmospheric profile...". Profile of what, temperature, CO_2, atomic oxygen, something else? Please clarify.
AC: The atmospheric model used for this sensitivity study is the midlatitude summer profile of temperature, pressure, and atomic oxygen VMR from MSIS-E-90 combined with WACCM CO_2 VMR profile for the midlatitude summer conditions. The corresponding information and the reference to MSIS-E-90 have been added to the text and to Fig. 1 caption.

RC: Section 3.1: You only discuss the atomic oxygen effect, but how good is the CO_2 abundance known? Please discuss how the uncertainty in CO_2 can effect the result.
AC: We have added the comparison of average CO_2(z) distributions for the ACE-FTS, WACCM, and SABER (Fig. 3a). We did not estimate the effects of different CO_2(z) profiles because a) the differences between the profiles are within standard deviation limits; b) the effects of CO_2 on I$_{15\mu m}$ radiance are bilateral (higher CO_2 VMR means more emitters for a given tangent height but more absorbers for the lower tangent heights); c) there is no "reference" CO_2(z) profile, which could be used instead of the SABER CO_2 VMR like lidar temperature, which substitutes the SABER T(z) distribution. On the other hand, using the "non-SABER" CO_2 profiles even for the estimates is not justified since they are not co-located with the SABER measurements and one can not introduce combined variable like γ because the problem is not linear on CO_2. Roughly, using the ACE-FTS CO_2(z) instead of the SABER CO_2(z) will reduce k$_{VT}$ above 100 km and increase it in the altitude range of 80–100 km; using the CRISTA CO_2(z) (not shown in Fig. 3a, see Fig. 1.1 in Rezac, 2011) will significantly increase k$_{VT}$ and its

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slope in the whole range of considered altitudes.

RC: Also, why T-dependence of k$_{VT}$ is neglected?
AC: Please, see our answer to the first general comment above.

RC: p. 32588, l. 27: This approach is valid only if I$_{15\mu m}$ depends linearly on γ, right? If so, this approach is likely not good for the mesosphere.
AC: Actually, in our approach we subdivide the problem of the k$_{VT}$ retrieval to two parts. Since k$_{VT}$ and atomic oxygen concentration are always used in combination in the statistical equilibrium equations for the ν_2 levels, we suggest using γ variable, which is the product of k$_{VT}$ and O(z). At this stage the real values of k$_{VT}$ or O(z) do not matter. Even if the I$_{15\mu m}$ does not depend linearly on γ, for each altitude there will be a single γ_{min} value, which minimizes the difference between the measured and simulated I$_{15\mu m}$ radiance. The interpretation of this value depends on real value of O(z). The quality of SABER O(z) is discussed below.

RC: 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.
AC: We agree with this point. Please, see the comment to the last question in the “General comments” section above. We have removed the reference to (Mlynczak et al., 2007) to avoid the confusion. We note that delta(t)<10 min criterion is always fulfilled.

RC: 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 k$_{VT}$ retrieval and so, the accuracy of the retrieved k$_{VT}$ is much less than that quoted in the paper. Please discuss this issue in more detail.
AC: There is increasing evidence for the reliability of the O determined from SABER.

Please, see the response to the first general comment of the Reviewer 2.

RC: p. 32591, l. 13: "... usually assumed that..." How good is this assumption?
AC: This assumption is good as long as the molecules and atoms obey the Maxwellian speed distribution, which is the case at the altitudes up to the exobase level (400–500 km). Please, also see the text (p. 32591, l. 20–23) with a reference to (Sharma et al., 1994).

RC: p. 32593, l. 6-7: "We show..." You didn't show, but suggest or speculate.
AC: This is correct. Indeed, we suggest the mechanism by saying that "We show that. . .the variation. . . ***may be*** explained", which implies that other variants are also possible.

RC: p. 32593, l. 12-15: This is not a practical recommendation. As long as new mechanisms for the CO_2 vibrational excitation are not revealed and rate constant for these mechanisms are not found, this recommendation can not be used in general circulation models.
AC: Actually, this recommendation is for the future and only if the mechanism we suggest is confirmed. As for the lines 15-16 "For the temperature retrievals from the 15 μm CO_2 atmospheric radiation observations, we recommend using values obtained in this work", we think that this recommendation is valid since applying the rate coefficient, which minimizes the differences between SABER and lidar, will move the retrieved temperatures closer to "reference" lidar temperatures. We agree that at the moment this is a technical correction because the detailed mechanism of $CO_2(\nu_2)$ excitation still needs understanding. However, using this value in the interpretation of 15μm CO_2 radiation will not lead to any temperature biases. On the contrary, temperature retrieval in the MLT will improve.

Technical corrections

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

AC: Most probably, this comment refers to line 23 on p. 32584. Fixed.

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

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

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

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