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Atmospheric Chemistry and Physics Discussions

Interactive comment on "$CO_2(\nu_2) - O quenching rate coefficient derived from coincidental SABE$

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We thank the Reviewer 2 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: While they account for the mapping of SABER pressure and temperature noise errors below 80 km, and the lidar temperature instrumental noise, they do not propagate the systematic errors of these quantities and, most importantly, the systematic uncertainties of the atomic oxygen derived from SABER.
AC: The quality of the SABER V1.07 product has been evaluated by Remsberg et al. (2008). As they show, in general, SABER V1.07 temperatures are 1–3 K higher than lidar in the lower stratosphere and 1–3 K lower than lidar in the upper stratosphere and

lower mesosphere. Assuming a 3 K positive temperature change in the lower stratosphere and 3 K negative temperature change in the upper stratosphere and lower mesosphere, we have estimated $I_{15\mu m}$ limb radiation change above 80 km. In this test performed for the mid-latitude atmospheric scenario, the pressure profile has been hydrostatically adjusted, the non-LTE populations have been found, and $I_{15\mu m}$ has been calculated and compared to $I_{15\mu m}$ calculated for unperturbed pressure/temperature distribution. This test shows that changes in $I_{15\mu m}$ above 80 km do not exceed 1%. At the same time, the sensitivity of $I_{15\mu m}$ to k_{VT} change shown in Fig. 1b of the manuscript is much higher: 17% at 90 km, 46% at 95 km, 73% at 100 km, 100% at 105 km, and 127% at 110 km. Correspondingly, the propagation of the systematic error in pressure/temperature distributions below 80 km to the area of our particular interest is negligible. These estimates have been added to the manuscript.
As for the atomic oxygen profile, one cannot speak about systematic errors since there are no "ground-truth" measurements, which could be used as a reference. This was partially the reason for providing the γ(z) profile so the k_{VT}(z) profile may be re-estimated in the future if the atomic oxygen profile is revised. However, there is increasing evidence for the reliability of the O determined from SABER. Here we cite three recent developments. 1) Xu et al (2012) determined the best model fit of vibrationally excited OH for the two OH emission bands observed by SABER (i.e., the 2.0μm band used by Smith et al. (2010) and the 1.6μm band also observed). They retrieved nighttime O profiles that were consistent with this model and found close agreement to the O profiles using only the 2.0μm band. Xu et al (2012) showed that the assumption of sudden death quenching of OH by O_2 could not simultaneously fit the observed emissions from the two channels. The sudden death quenching assumption was used in the retrieval of O from WINDII and may explain the large discrepancy between SABER and WINDII O amounts. 2) Mlynczak et al. (presentation at AGU fall meeting, 2011) showed that there is a near balance between heating and cooling in the MLT when all contributions are determined observationally from SABER and SORCE. The heating depends strongly on the O profile since chemical heating plays such a large role in

this region. A significant error in O would upset the balance. 3) Retrievals of O from OSIRIS (Sheese et al., 2011) are comparable to those from SABER and are similarly larger than the empirical MSIS values.

RC: The authors did not properly acknowledge previous work done on this area. Thus, Remsberg et al., JGR (2008) validated SABER temperatures and already compared them with the Lidars measurements at Fort Collins used in this work (see Sec. 5.3. pp. 22-24). They found a good agreement between the Fort Collins lidars temperatures and SABER temperatures when considering the estimated 50% error in the atomic oxygen concentration and the collisional rate coefficient K(CO_2-O) of 6e-12 cm3s-1 (see also Garcia-Comas et al., JGR, 2008). Hence, it is not surprising that the value the authors propose, 6.1e-12, is nearly identical to the value used in Remsberg et al. of 6.0e-12. The only difference is that the error bar proposed now is smaller, 30% instead of 50%, but this is explained because the authors did not include the systematic error in the atomic oxygen indirectly derived from the SABER OH and O_3 channels. Hence, what the authors are showing was essentially done before by comparing the SABER and Lidar temperatures.
AC: Indeed, Remsberg et al., (2008) performed the comparison of SABER versus lidar temperatures. However, the collocation criteria used in this work are rather loose: “5 degrees latitude, 10 degrees longitude, and 0.5 hours of the lidar hourly means centered on the half hour”. The atmospheric variability in the MLT area is quite strong and Remsberg et al. (2008) mentioned this problem in their paper. We already discussed the criteria necessary for profile-to-profile comparison (Feofilov et al., EGU General Assembly, Vienna, Austria, 2007). We show a couple of examples from this presentation here. As one can see in the following figure, http://dl.dropbox.com/u/44230060/temp_var.gif, the temporal variability of the MLT area is on the order of minutes and in some cases even 10 minute delay makes the profiles incomparable (compare the left-hand side plot which corresponds to 4 minutes difference between the measurements with the right-hand side plot which shows the same comparison but for the lidar measurement per-

formed 10 minutes later). The spatial variability is also important. As the figure http://dl.dropbox.com/u/44230060/spat_var.gif shows, even the measurements from the same lidar location made along Northern and Eastern beams may differ (and these beams are separated by less than 1 degree in the MLT). Because of these reasons we had to perform a thorough selection of the overlapping profiles using strict overlapping criteria and an updated lidar dataset, which made possible the comparison on the 10 minute timescale. Another difference of our approach compared to Remsberg et al. (2008) is treating all the altitudes separately. Initially, we used the same approach as Remsberg et al., (2008) and reported the results at the AGU Meeting in 2009. As one can see in the figure from this presentation, http://dl.dropbox.com/u/44230060/all_together.gif, the uncertainty in k_{VT} is quite large because of high scattering of the points. On the other hand, treating the altitudes separately and using the combined variable γ makes the minima in our Fig. 2a relatively narrow and well identifiable. We claim that the approach we used in this work is different from that utilized by Remsberg et al. (2008) even though both works deal with the same sets of measurements. Averaging “our” k_{VT} will provide the value close to k_{VT} obtained by Remsberg et al., (2008) but in our approach we have a) stricter overlapping criteria that give more confidence in the retrieved k_{VT} value; b) deeper insight in the physics of the MLT area. We have added a reference to Remsberg et al. (2008) and a brief discussion to the Section 1 of the manuscript.

RC: The authors should have used the individual O profile derived in each of the coincidences (individual radiance calculations) when deriving each of the single collisional rate values. In principle, if the problem is linear, one would not expect significant changes in the mean value, however, there will be in the estimated standard deviation.
AC: This is correct, and the approaches are almost equivalent. Actually, we started with the suggested approach but later we switched to the one described in the paper since the minima for the average ζ curves are better defined. Estimating of the standard deviation in this case is made using ζ curves in Fig.2a.

RC: The proposed mechanism for the altitude dependence of the rate coefficient is very attractive but very speculative and it does not deserve 40 lines of text. The reader would like to see some estimations (even "back of the envelope" estimations) of the concentration of hot O and how compares K_hot*[O_hot] with K*[O]. I suggest to remove the whole paragraph if no estimations can be provided or to reduce it if they are given.
AC: We have added the "back of the envelope" estimates to the discussion. However, we do not see how one can shorten the paragraph without losing the steps necessary for understanding the problem in general and the suggested formula (5) in particular. Moreover, we had to add a sentence describing other potential sources of CO_2(v2) pumping suggested by the Reviewer 3.

RC: On the other hand, it surprises that the authors did not invoke a probably more likely reason: the temperature dependency of K(CO_2-O). Its altitude dependency resembles very much that of the temperature profile.
AC: Indeed, this could be a plausible explanation since the theoretical studies (de Lara-Castells et al., 2006) support ***positive*** temperature dependency of k_{VT}. One has to keep in mind, though, that in the present study we already used a standard $(T/300)^{1/2}$ temperature scaling of k_{VT}, so one has to assume that the temperature dependency is stronger than $T^{1/2}$. However, the most recent laboratory measurements of k_{VT} in the 142–490 K temperature range (Castle et al., 2012) demonstrate ***negative*** temperature dependency of k_{VT}. In principle, assuming that the V-T collisional process in the laboratory is equivalent to the collision in the atmosphere, one has to use the measured temperature dependency. Figure 3b shows the estimates for $k_{VT}(z)$ made with negative temperature dependency. The corresponding discussion has been added to the text.

RC: In the review of K(CO_2-O) measurements (Table 1) a key atmospheric derivation is missing, that done using ATMOS measurements (Lopez-Puertas et al., 1992). This is one of the most comprehensive derivation since there were measured, simultane-

ously, all the key magnitudes (pressure, kinetic temperature, CO_2 VMR, and CO_2 (010) vibrational temperature) except the atomic oxygen.
AC: We have added the reference to the table for the completeness of the historical review. However, the accuracy of k_{VT} retrieved without measuring atomic oxygen can not be high since atomic oxygen is a variable component, and climatological or model value may differ from the real situation in the atmosphere. Lopez-Puertas et al. (1992) address this point and discuss the results obtained with O(z) retrieved from MSISE-90 and CIRA-86, and the value of k_{VT} estimated in this work, varies from 3.0×10^{12} cm^3 s^{-1} to 6.0×10^{-12} cm^3 s^{-1}. This example illustrates the importance of simultaneous measurement of O(z) along with CO_2(z), and $I_{15\mu m}(z)$ for adequate interpretations of radiance measurements.

RC: Since the review also cover theoretical studies, it might also be worthwhile to mention the study by De Lara et al., J. Chem. Phys., 2006.
AC: We agree with that and we have added the reference to de Lara-Castells et al. (2006) to the discussion section.

Additional references

Sheese, P. E., I. C. McDade, R. L. Gattinger, and E. J. Llewellyn (2011), Atomic oxygen densities retrieved from Optical Spectrograph and Infrared Imaging System observations of O_2 A-band airglow emission in the mesosphere and lower thermosphere, J. Geophys. Res., 116, D01303, doi:10.1029/2010JD014640. Xu, J., Gao, H., Smith, A., K., Zhu, Y. (2012), Using TIMED/SABER nightglow observations to investigate hydroxyl emission mechanisms in the mesopause region, J. Geophys. Res., 117, D02301, doi:10.1029/2011JD016342.

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