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## COMMENT

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This article is a comment on Ozak et al. (2016), <https://doi.org/10.1002/2015JE004871> and is replied to by Ozak et al. (2017), <https://doi.org/10.1002/2017JE005389>.

This Comment and Reply pair resolves any need for a correction to be made to paper <https://doi.org/10.1002/2015JE004871> by Ozak et al., which now includes a relevant erratum statement directing readers to the Comment and Reply.

**Key Points:**

- Calculations of CO<sub>2</sub> line mixing by Ozak et al. (2016) were affected by a wrong choice of the broadening species (air instead of CO<sub>2</sub>)
- Line mixing model for pure CO<sub>2</sub> leads to early Mars surface temperatures very close to those obtained with the usual  $\chi$  factor corrections

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## Comment on "Radiative Transfer in CO<sub>2</sub>-Rich Atmospheres: 1. Collisional Line Mixing Implies a Colder Early Mars"

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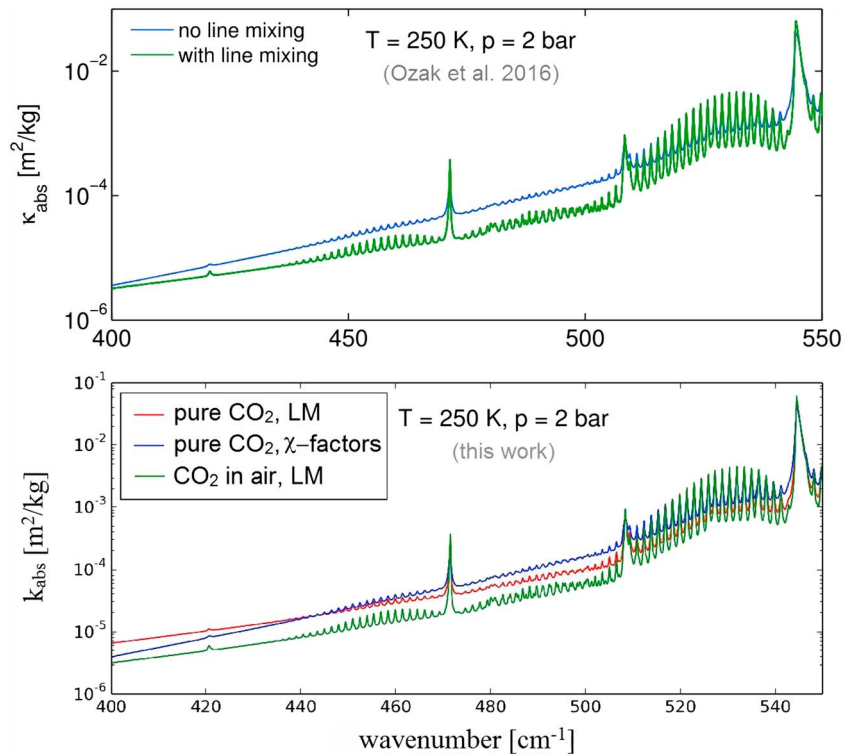
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**Abstract** Ozak et al. (2016) claimed that explicitly including the effect of CO<sub>2</sub> collisional line mixing in their radiative transfer calculations yield CO<sub>2</sub> atmospheres that are more transparent to infrared radiation than when spectra calculations are made using sub-Lorentzian line shapes. This would in particular imply significantly colder surface temperatures (up to 15 K) for early Mars than estimated in previous studies. Here we show that the relative cooling that Ozak et al. (2016) associated to the effect of collisional line mixing is in fact due to a wrong choice of broadening species (air instead of CO<sub>2</sub>). We then calculated line-by-line spectra of pure CO<sub>2</sub> atmospheres using a line-mixing model developed for self-broadened CO<sub>2</sub>. Using the LMD Generic model (in 1-D radiative-convective mode), we find that calculations made with the proper collisional line mixing model and with sub-Lorentzian line shapes lead to differences between early Mars surface temperatures smaller than 2 K only.

### 1. Main Text

We first introduce here the various spectroscopic terms needed for the reader to understand the content of this comment. Modeling the entire CO<sub>2</sub> "allowed" spectrum (i.e., due to the molecule dipole and not to collision-induced absorption), including both the regions near the lines centers and the far wings, is an extremely difficult task for which no rigorous model is available so far. The measured spectrum can be significantly different from that calculated with the usual Lorentz (or Voigt) profile, due to two effects that are neglected by this profile. The first one, called line mixing, is associated with the collisional transfers of rotational populations between absorption lines. It modifies the shape of clusters of closely spaced lines and results in transfers of absorption from the band wing region to the band center (Hartmann et al., 2008) leading to the strongly sub-Lorentzian behavior observed in CO<sub>2</sub> band wings. The second effect, related to the finite duration of collisions, affects the absorption in the far wings of the lines only (Hartmann et al., 2008). To model CO<sub>2</sub> absorption spectral shape, two approaches are commonly used. In the first, called the  $\chi$  factor approach, an empirical correction of the Lorentzian shape is adjusted to laboratory measurements of the absorption in some band wings (e.g., at 4.3  $\mu\text{m}$  in Perrin & Hartmann, 1989). The effects of both line mixing and the finite collision duration are thus taken into account by this approach, but for the considered band wings region only. In the absence of precise and available data for other spectral region, the same  $\chi$  factor correction is generally used for all other CO<sub>2</sub> bands. In addition to this approximation, the effect of line mixing in the band center is not taken into account by the  $\chi$  factor correction. The second approach, based on the use of the impact and the energy-corrected sudden approximations (Tran et al., 2011, and references therein), takes line mixing into account but not the effect of finite duration of collisions. This model, self-consistent for all bands, leads to satisfactory agreement with laboratory measurements for various bands, at different pressure and temperature conditions (Tran et al., 2011). Very accurate predictions are obtained in the central regions of the bands with discrepancies that may increase together with the breakdown of the impact approximation (Hartmann et al., 2008), when going far away in the wings. The line mixing and the  $\chi$  factor approaches are thus fully different and rely on completely different approximations. Yet they can both be used to model broad band CO<sub>2</sub> absorption spectra.

Ozak et al. (2016, hereafter, OZ16) explored the effect of using the line-mixing (hereafter, LM) approach in CO<sub>2</sub>-dominated atmospheres, typical of the early Martian environment (see review by Forget et al., 2013). They found that, using a 1-D radiative-convective model, the use of the LM approach results in colder early Mars surface temperatures than those obtained with the  $\chi$  factor approach. Note that as mentioned above,

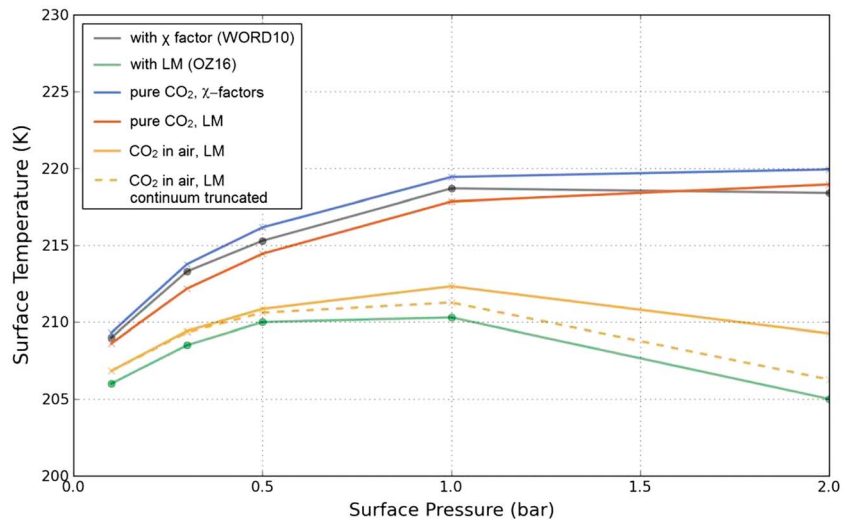


**Figure 1.** Line-by-line absorption spectra of a pure CO<sub>2</sub> atmosphere, at a temperature of 250 K and a pressure of 2 bars. (top) Figure directly imported from OZ16, calculated with their  $\chi$  factors corrections (blue) or with their (green) inclusion of CO<sub>2</sub>-in-air line mixing (LM). (bottom) For comparison, we plotted three spectra calculated under the same pressure and temperature condition: In blue is the calculation with our  $\chi$  factors, in green calculation with our CO<sub>2</sub>-in-air line mixing, which both match the curves of OZ16, and in red our pure CO<sub>2</sub> line mixing. Absorption coefficient unit is in  $\text{m}^2 \text{kg}^{-1}$ , as in OZ16. Note that contribution of pure CO<sub>2</sub> continuum is not included here.

LM effects on the line wings are already taken into account in the spectral calculations using the  $\chi$  factor approach; therefore, one cannot state that these calculations correspond to the case of “no line mixing,” as done in OZ16. For instance, for a pure CO<sub>2</sub> atmosphere with a surface pressure of 2 bars, OZ16 reported that surface temperatures could be lowered by about 15 K compared to previous studies (Wordsworth et al., 2010) in which the  $\chi$  factor approach was used. Such a result would have profound implications for the early Mars enigma (Haberle et al., 2017, chap. 17; Wordsworth, 2016), making the formation of ancient valley networks and lakes even more difficult to explain.

However, here we show that this cooling is due to an improper choice of the LM model. OZ16 used the updated version (Lamouroux et al., 2010) of the LM approach database and software package of Niro et al. (2005), built for Earth atmosphere studies, that is, for CO<sub>2</sub> broadened by air and not for pure CO<sub>2</sub>, as needed for the case of early Mars. Here we instead use the LM package devoted to pure CO<sub>2</sub>, developed by Tran et al. (2011) and updated in Kassi et al. (2015), to calculate absorption spectra of pure CO<sub>2</sub> under various pressure and temperature conditions typical of the early Martian environment.

An example of our calculated spectra is shown in Figure 1 in which those obtained by OZ16 are also reported for comparison. As in OZ16, we performed two calculations: the first with the LM approach but using the package of Tran et al. (2011) and Kassi et al. (2015) for pure CO<sub>2</sub> (hereafter denoted by pure CO<sub>2</sub> LM, in red). In the second calculation, the  $\chi$  factor approach for pure CO<sub>2</sub> (Perrin & Hartmann, 1989) was used (in blue). Note that the latter is the widely adopted procedure to calculate absorptions for early Martian CO<sub>2</sub>-dominated atmospheres (Mischna et al., 2012; Wordsworth et al., 2010). Finally, we also calculated spectra, as done by OZ16, with CO<sub>2</sub>-in-air LM by using the package of Niro et al. (2005) and Lamouroux et al. (2010) (in green). Figure 1 calls for two remarks. First, our calculations with CO<sub>2</sub>-in-air LM and with the pure CO<sub>2</sub>  $\chi$  factor approach agree very well with those of OZ16. The second and very important remark is that



**Figure 2.** Temperatures at the surface of a pure CO<sub>2</sub> atmosphere of various thicknesses, exposed to early Mars conditions and computed with the LMD Generic model, with pure CO<sub>2</sub> LM (red), and with the  $\chi$  factors corrections (blue). Orange lines correspond to calculations using CO<sub>2</sub>-in-air LM with pure CO<sub>2</sub> continuum truncated (dashed line) or not (solid line). For comparison, we plotted in black the original curve from Wordsworth et al. (2010) ( $\chi$  factors), and in green the one from OZ16 (with CO<sub>2</sub>-in-air LM). Calculations include CO<sub>2</sub> condensation. Mean incident flux at the top of atmosphere is  $442 \text{ W m}^{-2}$ .

when using the correct collision partner, that is, pure CO<sub>2</sub> LM, the obtained spectrum (red) is closer to that calculated with the pure CO<sub>2</sub>  $\chi$  factor approach (blue), with respect to the CO<sub>2</sub>-in-air LM calculation (green).

Using the LMD Generic model (in 1-D time-marching radiative-convective mode) parameterized following OZ16, with the two spectral calculation approaches for pure CO<sub>2</sub> (i.e., LM and  $\chi$  factor), we performed numerical simulations of pure CO<sub>2</sub> atmospheres of various thicknesses (from 0.1 to 2 bars), under Noachian Mars conditions as in OZ16. Pure CO<sub>2</sub> continuum was taken into account in the two calculations. Specifically, the CO<sub>2</sub>-CO<sub>2</sub> far-infrared collision-induced absorptions (CIAs) from Gruszka and Borysow (1997) and CIA and dimer absorptions from Baranov et al. (2004) were used and extrapolated for the whole spectral range, as widely done by previous studies and in particular by Wordsworth et al. (2010). Figure 2 shows the equilibrium surface temperatures obtained with (red) pure CO<sub>2</sub> LM and with (blue) the pure CO<sub>2</sub>  $\chi$  factor approach. For comparison, the results obtained by OZ16 using CO<sub>2</sub>-in-air LM (green) and those obtained in Wordsworth et al. (2010) (black) in which  $\chi$  factors were used were also plotted. In addition, we also performed simulations using CO<sub>2</sub>-in-air LM. For this case, two calculations were made. In the first (solid orange line), pure CO<sub>2</sub> continuum was calculated as mentioned above, that is, extrapolated for the whole spectral range. In the second, the same data were used but were truncated at  $250 \text{ cm}^{-1}$  for far-infrared CIA and between  $1200$  and  $1600 \text{ cm}^{-1}$  for CIA and dimer absorptions from Baranov et al. (2004), respectively, as done in OZ16 (dashed orange line). As can be observed in Figure 2, the result of this latter is in very good agreement with that of OZ16, indicating that the 1-D radiative-convective version of our LMD Generic model agree well with the one developed by OZ16. The correlated- $k$  radiative transfer model of OZ16 is thus not concerned by our comment and could be used for radiative transfer in planetary atmospheres.

Firstly, as can be observed, our simulations with the  $\chi$  factor approach (blue) agree well ( $\pm 2 \text{ K}$ ) with those of Wordsworth et al. (2010) confirming the calculation procedure we used. The remaining difference is likely due to the spectroscopic data used in the two calculations. Wordsworth et al. (2010) used data from HITRAN 2004 (Rothman et al., 2005), while in our calculations, HITRAN 2012 was used (Rothman et al., 2013). Second, surface temperatures obtained with pure CO<sub>2</sub> LM and pure CO<sub>2</sub>  $\chi$  factors are very close to each other, the differences being always smaller than 2 K for all considered surface pressures. This is consistent with the fact that absorptions calculated with pure CO<sub>2</sub> LM are very close to those calculated with the  $\chi$  factors in the most relevant infrared spectral regions for early Mars, as shown in Figure 1. This is also consistent with the fact that LM effects on the line wings are by nature already taken into account in the  $\chi$  factor

approach. In the opposite, high-resolution spectra with CO<sub>2</sub>-in-air LM (green, see Figure 1) being more transparent in infrared regions, surface temperatures obtained in this case can be much lower (up to 10 K, solid orange line in Figure 2). Note that in addition to the effect of the wrong broadening species, due to the effect of pure CO<sub>2</sub> continuum truncation, OZ16 obtained even lower surface temperature (dashed orange and green lines in Figure 2).

In summary, the significant cooling reported in Ozak et al. (2016) is mostly due to a wrong choice of broadening species (air instead of CO<sub>2</sub>). Moreover, we show that early Mars surface temperatures calculated when using the proper LM model are very close to those obtained from spectra calculations based on the “usual”  $\chi$  factor approach, their differences being smaller than 2 K, and thus within the uncertainty of usual early Mars radiative transfer calculations (Ozak et al., 2016, Figure 2). This very good agreement thus justifies the use of the usual  $\chi$  factor approach for early Mars climate studies. This work also stresses the need for accurate spectroscopic data for early Mars pressure and temperature conditions, as well as for their careful use.

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