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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Investigations of the photochemical isotope equilibrium between O_2, CO_2 and O_3" *by* R. Shaheen et al.

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At first sight it seems easy to mix some CO2 and O2 and switch on the light, yet this paper shows some of the complexities. Although this paper is not the last word hopefully (these are quite fundamental gases for life), in the sequence of attempts to understand the isotope exchange processes, it is the most comprehensive careful set of tests, described in a well written manuscript that also carefully deals with what other experimenters have found over the years. The model developed is useful in better understanding and comparing experiments. Note that in the table 2, slope is based on single points, and not the evolution of a mixure in time. This may be of relevance when

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comparing to stratopsheric conditions. It is interesting that CO2, a gas that does not exchange oxygen atoms unless it sees water..can show such an activity when O(1D) is around supplied in this case by the photolysis of ozone. The earlier experiments often were described in terms of "slopes" only, which has lead to some confusion. It is important that those who conducted similar experiments scrutinize the explanations and interpretations presented in the present paper. Concerning the experiments the authors could perhaps state how much ozone was present in the different experiments. (for future experiments also please mention that ozone is not stable and great care has to be taken). Ozone is the agent that carries the enrichment, and it would be useful to know something about the ozone levels. Furthermore, it is written that ozone is removed over hot nickel. Because nickel is a metal with a wide range of catalytical properties, could it have occurred that CO2 exchanged O atoms on the nickel deposited there through the decomposition of ozone ? Nickel tarnishes in ozone as a result of contact with ozone. Concerning the findings, one central question is "is the isotopic composition of the CO2 after the reaction mass independent solely because ozone has a mass independent isotopic composition, or..is there an additional mass independent isotope exchange process at work in the reaction O + CO2 ? Do the experiments allow a conclusion in this sense ? It is noted that not all experiments conducted pertain to stratopsheric conditions, and high CO2 levels do show a big effect, but apparantly cannot help to find out why the slope in the stratopshere is 1.7. It is suggested by the referee to include a small figure showing tropospheric O2, CO2, and stratopsheric CO2, O3 and the value expected based on the present experiments, showing the gap to be explained in the future. Finally, one statement may seem a bit confusing, and the authors are invited to comment. It is written twice (as a conclusion) that "the CO2 isotopic composition at photochemical equilibrium is independent of the initial O2 and CO2 isotopic composition" This may puzzle non isotope experts because when there is no 18O in the intial CO2 and O2, there will be no 18O in the final CO2. Therefore the isotopic composition does matter. When there are 2 reservoirs, namely CO2 and O2, and isotope exchange is invoked between them via a certain agent (mechanism), and

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equilibrium is achieved, we expect the final isotopic composition to depend on the initial isotopic composition. We do not expect the isotopic composition to play a role as such, because at the low abundaces used, the isotopes act as tracers. Would it be different when highly enriched mixtures are used (e.g. 50 % 18O)?, as this changes the physics of the system in various ways. For instance the quenching properties may be affected. I think this point should be clarified to keep up our appetite for more isotope work.

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