

## ***Interactive comment on “Investigations of the photochemical isotope equilibrium between O<sub>2</sub>, CO<sub>2</sub> and O<sub>3</sub>” by R. Shaheen et al.***

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We thank Carl Brenninkmeijer for his thoughtful comments and suggestions. Before we discuss the five points raised in his report in some detail, we would like to specify his statement that “in Table 2, the slope is based on single points, and not the evolution of a mixture in time”.

The data from *our new experiments* reported in this paper, lines 1-6 of Table 2, report slopes that were determined from time evolutions and not from the equilibrium point only. This also holds for the measurements of Chakraborty and Bhattacharya (2003) listed in lines 16-18. The situation is different, however, for the data presented in lines 7-15 (Johnston et al (2000) and Wen & Thiemens (1993)). For those experiments no

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data for the time evolution is available and only the initial and final isotope compositions were used to determine the observed slopes. These slope values are therefore based on two points rather than on only one data point.

### 1. Ozone Content

Due to the remaining vapour pressure of O<sub>3</sub> at liquid nitrogen temperature, O<sub>3</sub> cannot be trapped quantitatively in a liquid nitrogen cooled trap, where the vapour pressure is around 0.2 Pa. Therefore, we unfortunately have not been able to reliably quantify O<sub>3</sub> concentrations in our experiments and have only two rather qualitative remarks. 1) In most of the experiments we observed a slight blue colour in the CO<sub>2</sub> trap, which is indicative of O<sub>3</sub>. 2) The isotope mass balance, i.e.,  $c(\text{CO}_2)_i \delta(\text{CO}_2)_i + c(\text{O}_2)_i \delta(\text{O}_2)_i - c(\text{CO}_2)_f \delta(\text{CO}_2)_f - c(\text{O}_2)_f \delta(\text{O}_2)_f$ , where  $c$  denotes the concentration,  $\delta$  the delta value and the indices  $i$  and  $f$  the initial and final values, was in the case of the oxygen dominated mixture ( $\rho \sim 120$ ) closed within 0.25 per mil  $\pm$  0.35 per mil ( $2 \sigma$ ). Given that O<sub>3</sub> is about 100 per mil enriched relative to O<sub>2</sub>, this indicates that O<sub>3</sub> levels were at most 0.25% of O<sub>2</sub> levels, corresponding to a partial pressure of (60  $\pm$  80) Pa

### 2. Effect of Ni

The effect of the decomposition of O<sub>3</sub> on a Ni surface was investigated in detail in [Johnston *et al.*, 2000]. In that study the authors indeed determined a slight enrichment in CO<sub>2</sub> from the decomposition of O<sub>3</sub> on Ni, which amounted to 2-3 per mil for  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ . However, in those test experiments the amount of O<sub>3</sub> exceeded that of CO<sub>2</sub>, which is due to the high O<sub>2</sub>/CO<sub>2</sub> ratios applied for some experiments in that study. We have used lower O<sub>2</sub>/CO<sub>2</sub> ratios, and based on the O<sub>3</sub>/O<sub>2</sub> ratio of <1% (see above) we expect that the O<sub>3</sub>/CO<sub>2</sub> ratio was about one order of magnitude lower than that tested in [Johnston *et al.*, 2000]. Therefore, the effect of Ni is most likely negligible for our experiments.

### 3. Mass independent fractionation in O(<sup>1</sup>D)+CO<sub>2</sub>

We have indeed reported one experimental result that is a strong indication for a fractionation in the  $O(^1D)+CO_2$  exchange process, namely the  $\rho$  dependence of the experimental results. The equilibrium enrichments change in a non mass dependent fashion with  $\rho$ . According to our understanding of the ozone isotope enrichments, this cannot originate from  $O_3$  and thus it indicates non mass dependent fractionation in the exchange process itself. This is explained on page 7883, top, and we will clarify this point further in the revised version.

#### 4. Additional figure

We have incorporated an additional figure in the revised manuscript that shows our results translated to the stratospheric situation.

#### 5. Effect of isotope composition

We are thankful for the comment on our statement that the isotope composition of  $CO_2$  at photochemical isotope equilibrium with oxygen and ozone is independent of the initial isotopic composition of  $CO_2$  and  $O_2$  used. The question of the referee was the incentive for us to elaborate a bit on this statement.

First, we note that the case mentioned by the referee, namely the hypothetical case of  $CO_2$  and  $O_2$  without  $^{18}O$ , may itself be a bit confusing, because in this case one would not need to carry out isotope exchange experiments in the first place.

However, we did not discuss in the original manuscript that our conclusion only holds for isotope mixtures of near-natural heavy isotope abundance (which includes the normal or anomalous enrichments of the order of few hundred per mil as used in our paper). The limit to the statement is that the isotope chemistry should be determined by singly substituted species only, e.g.,  $^{18}O$  should only be produced by singly substituted  $O_3$ . In strongly enriched mixtures, a departure from this behavior is expected. For example, in 50:50 mixtures of  $^{16}O$  and  $^{18}O$ , the isotopomer enrichment of equilibrated  $^{50}O_3$  and  $^{52}O_3$  is almost equal, i.e.,  $E(50) = E(52) \sim 10\%$  and  $E(54) \sim E(48) = 0\%$  (Mauersberger

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et al. 1993 (Geophys. Res. Lett. 20, 1031), Janssen et al. 2003 (Chem. Phys. Lett. 367, 34)). Considering only isotope effects due to the abundance of O<sub>3</sub> molecules, <sup>48</sup>O<sub>3</sub> and <sup>54</sup>O<sub>3</sub> produce O(<sup>1</sup>D) and Q(<sup>1</sup>D) (where Q = <sup>18</sup>O) at equal amounts. <sup>50</sup>O<sub>3</sub> and <sup>52</sup>O<sub>3</sub> do the same. Therefore, the expected Q/O ratio is 1 and Q(<sup>1</sup>D) will not be enriched. This is different from natural oxygen mixtures, where Q(<sup>1</sup>D) comes from <sup>50</sup>O<sub>3</sub> only. Since that is enriched, Q(<sup>1</sup>D) will be too.

In addition – though likely smaller in magnitude – there are even more factors that could cause a dependence on the initial isotopic composition when changing the isotope composition of the reactants from slightly to heavily enriched: isotope dependent quenching efficiencies of O(<sup>1</sup>D) and CO<sub>3</sub><sup>\*</sup>, ozone isotopomer dependent photolysis rates and mass dependent rates of the O(<sup>1</sup>D) + CO<sub>2</sub> reaction, which would include reactions with CQ<sub>2</sub>, for example.

We have included this discussion in the revised version of our manuscript.

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