

Interactive  
Comment

## ***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.***

**M. Miller (Referee)**

mfm@bas.ac.uk

Received and published: 26 September 2006

### **General Comments:**

Occasionally one encounters manuscripts which are authoritative, very well written, and present findings which clearly represent a significant advancement of knowledge in the respective field. Such is the case with the *Shaheen et al.* article. There is a substantial amount of information presented in this manuscript, and this reviewer found it necessary to read the manuscript several times – especially the *Discussion* section – in order to appreciate some of the arguments and logic presented.

The manuscript describes and discusses novel, room-temperature experiments de-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

vised to investigate the unusual isotopic behaviour of UV-irradiated O<sub>2</sub>-CO<sub>2</sub> and O<sub>3</sub>-CO<sub>2</sub> mixtures at secular equilibrium, to gain further insight to the O(<sup>1</sup>D)-mediated isotope transfer between O<sub>3</sub> and CO<sub>2</sub>. It has been recognised for some considerable time that the transfer of the attendant 'non-mass dependent' isotopic anomaly from O<sub>3</sub> to CO<sub>2</sub> is of considerable importance in the context of understanding the origin of the unusual isotopic composition of stratospheric CO<sub>2</sub>. As the authors admit, their paper does not offer an explanation for the remarkable slope of 1.7 on the oxygen three-isotope plot as given by stratospheric CO<sub>2</sub>; the origin of that phenomenon thus remains unknown. However, in this paper, the authors demonstrate the surprising finding that the oxygen isotopic composition of CO<sub>2</sub> at photochemical equilibrium is not dependent on the isotopic composition of the reactants.

This appears to be the first study of the isotopic characteristics of the secular equilibrium point, rather than investigating solely the three-isotope fractionation line slope of the system. Furthermore, the authors show that knowledge of the isotope equilibrium point enables the slope value to be calculated anyway, from the isotopic composition of the reactants. They also suggest, with good reason, that future investigations to identify the mechanisms responsible for the extraordinary isotopic composition of stratospheric ozone will need to include additional physical parameters such as temperature and also different wavelengths of the UV irradiation used for ozone photolysis. Although not referred to by the authors, it would also be instructive for future investigations to see whether the presence of molecular nitrogen (introduced preferably as the most abundant constituent in the reactant mixture, thereby providing a more realistic model of stratospheric conditions) has an influential effect on the oxygen isotope distributions.

### Specific Comments:

There is really only one substantive point that I feel the authors should be invited to comment on, and preferably address. Additionally, there a number of minor points of clarification which should be attended to, together with the correction of the few typographic errors that were identified.

The substantive point relates to the information presented in Figure 2. Although the arrays showing the isotopic evolution of CO<sub>2</sub>-O<sub>2</sub> mixtures (Fig. 2a) and CO<sub>2</sub>-O<sub>3</sub> mixtures (Fig. 2b) are impressively linear, I am concerned that the respective  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  data are all reported relative to the instantaneous isotopic composition of molecular oxygen in the mixture. Thus, all the data points are essentially reported to different isotopic references (of unspecified compositions). This is not really a correct use of the  $\delta$  notation and does not allow meaningful comparisons to be made. I would prefer to see the isotopic data reported relative to a recognised reference material such as VSMOW, even if those results were presented as a separate Figure and Table, rather than being shown in Fig. 2.

### Technical corrections:

Other, relatively minor, points are as follows, given in the order in which they occur in the manuscript:

#### Section 1, Introduction:

- (i). Stratospheric CO<sub>2</sub> $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values of 45 per mil and 54.9 per mil are stated, for the highest altitude (60 km) measurements made so far. It would be helpful to quote the reference, as  $\delta^{17}\text{O} < \delta^{18}\text{O}$  in this case and those results are not at all in accord with the 1.7 fractionation line reported by Lämmerzahl et al. (2002). The maximum altitude sampled in the latter work was 33 km.
- (ii). Lämmerzahl et al. (2002) reported stratospheric CO<sub>2</sub> $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values relative to tropospheric CO<sub>2</sub>, not to air O<sub>2</sub> (as stated by Shaheen et al.).
- (iii). It would be helpful if a definition was provided of the parameter  $\gamma$ , as used in the expression for the branching ratio  $\gamma/(1 - \gamma)$ .
- (iv). In the final paragraph of this section, the second sentence states that ‘The iso-electronic isotope exchange reaction (R4) could possibly influence the isotopic

composition of  $O(1D)$ . But R4 is not an isotope exchange reaction; it is the decomposition pathway of the  $CO_3^*$  entity. Furthermore, there seems to be no reason to use the term 'iso-electronic' in this context.

## Section 2.2, Preparation of enriched $CO_2$ :

- (v). In the final paragraph of this Section, it is stated that: 'The accuracy of the  $\delta$  values for the starting  $CO_2$  material is 0.2 and 0.1 per mil for  $^{17}O$  and  $^{18}O$ , respectively.' But there is no mention of how those values were measured to this level of accuracy. If the  $\delta^{17}O$  data were obtained using the Assonov and Breninkmeijer (2001) method, then (as stated in Section 2.3) the  $2\sigma$  analytical error is no better than 0.6 per mil.

## Section 2.4, Blank experiments:

- (vi). Similar to the previous comment, it is seen in the final paragraph of this Section that 'a small fractionation for  $CO_2$  ( $\delta^{17}O=0.4$  per mil' is stated. Again, if the  $\delta^{17}O$  data were obtained using the Assonov and Breninkmeijer (2001) method, then the  $2\sigma$  analytical error is no better than 0.6 per mil.

## Section 3, Results:

- (vii). Was there a particular reason for choosing the composition of the reactant mixture to be  $(64\pm 1) \mu\text{mol } CO_2$  and  $(800\pm 10) \mu\text{mol } O_2$ ? It would also be helpful to have mentioned the total pressure in the reactor, although admittedly that can be obtained from the information given. A simple calculation indicated that the pressure was about 80 hPa.

(viii). It would be helpful to define what is meant by the ‘e-folding time of the equilibration process’. The same terminology is also used in the caption to Table 1.

### Section 3.1, Photochemical Isotope Equilibrium:

- (ix). Commencement of the second paragraph: it should be stated whether the small or large reactor was used and hence what the corresponding pressure was. Similarly, with regard to the second set of experiments (as mentioned at the beginning of the third paragraph).
- (x). With regard to the decision to report the isotopic composition of the  $\text{CO}_2$  with reference to that of the coexisting  $\text{O}_2$ , please refer to my comment (‘substantive point’) given above.

### Section 3.2, Dependence on $[\text{O}_2]/[\text{CO}_2]$ :

- (xi). Referring to equation (2): nowhere in the manuscript could I find the definition of the parameter  $\rho_0$ . It is important that this omission is rectified.

### Section 4.1, Dependence on $[\text{O}_2]/[\text{CO}_2]$ :

- (xii). First sentence: ‘Our experiments with varying the  $\text{O}_2/\text{CO}_2$  ratio at constant pressure show that the equilibrium enrichments in  $\text{CO}_2$  decrease when the  $\text{CO}_2$  content exceeds 5%.’ I think that what the authors meant to say is that the  $^{17}\text{O}$  and  $^{18}\text{O}$  equilibrium enrichments in  $\text{CO}_2$  decrease when the  $\text{CO}_2$  content exceeds 5%.

Fig. 1 caption:

(xiii). There are no isotope *enrichments* in O<sub>2</sub> indicated by the Figure, only *depletions* of <sup>17</sup>O and <sup>18</sup>O. The caption should perhaps read ‘Oxygen isotope changes in O<sub>2</sub> (squares) and CO<sub>2</sub> (circles)...’

Typographic errors noted in the manuscript:

(xiv). Section 1, line 22: ‘45 per mil and 54.9 per mil’

(xv). Page 2, second column, second paragraph: ‘UV-irradited’

(xvi). Page 7, first column, line 15: ‘CO<sub>2</sub>.’

(xvii). Final sentence of the acknowledgements section: ‘... who enabled *her* to complete this work.’

---

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7869, 2006.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)