

## Reply to comment by Röckmann and Kaiser on “Evidence for O-atom exchange in the $O(^1D) + N_2O$ reaction as the source of mass-independent isotopic fractionation in atmospheric $N_2O$ ”

Yuk L. Yung, Mao-Chang Liang, and Geoffrey A. Blake

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, USA

Richard P. Muller

Computational Materials and Molecular Biology, Sandia National Laboratories, Albuquerque, New Mexico, USA

Charles E. Miller

Atmospheric Chemistry Element, Jet Propulsion Laboratory, Pasadena, California, USA

Received 9 February 2005; revised 5 April 2005; accepted 10 May 2005; published 10 June 2005.

**Citation:** Yung, Y. L., M.-C. Liang, G. A. Blake, R. P. Muller, and C. E. Miller (2005), Reply to comment by Röckmann and Kaiser on “Evidence for O-atom exchange in the  $O(^1D) + N_2O$  reaction as the source of mass-independent isotopic fractionation in atmospheric  $N_2O$ ,” *Geophys. Res. Lett.*, 32, L11808, doi:10.1029/2005GL022669.

### 1. On the Isotopic Exchange of $O(^1D)$ and $N_2O$

[1] Based upon the authors’ questioning of the existence of the  $C_{2v}$  intermediate, we have reviewed our evidence for the existence of this state. It now appears that this state was in fact an artifact of our calculation [Yung *et al.*, 2004], and was a saddle point rather than a true minimum. Our desire to provide a timely response to this criticism has kept us from determining exactly what minimum structure will be obtained by a full minimization at the level of theory employed. However, it is clear that the  $C_{2v}$  symmetry of the compound is broken in such a way that the two N-O bonds are no longer equivalent. We are grateful to the authors for helping us resolve this issue.

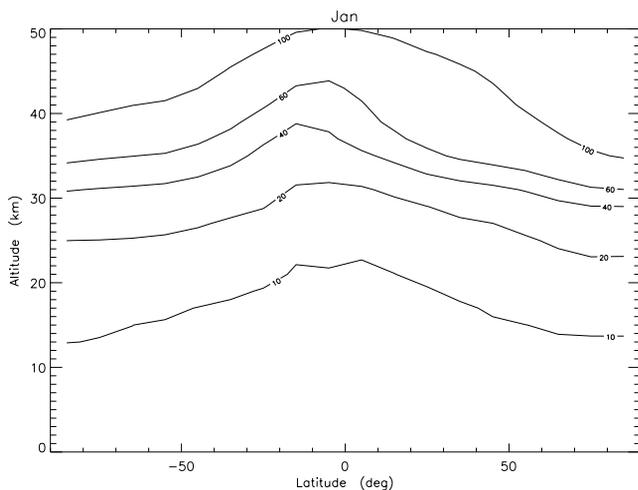
[2] We further note that new laboratory studies of the  $O(^1D) + N_2O$  reaction [Nishida *et al.*, 2004] show that the inelastic channel ( $O(^1D) + N_2O \rightarrow O(^3P) + N_2O$ ) is about 5% that of the reactive channels ( $2NO$  and  $N_2+O_2$ ). Based on the facts that  $CO_2$  and  $N_2O$  are isoelectronic linear triatomic molecules and that their overall rates for the reaction with  $O(^1D)$  are comparable, it is reasonable to assume that the nominally ‘non-reactive’ reactions in the two systems have similar probabilities for oxygen atom isotopic exchange. By analogy with  $O(^1D) + CO_2$  reactions [Perri *et al.*, 2003], the branching ratio of the elastic channel for ( $O(^1D) + N_2O \rightarrow O(^1D) + N_2O$ ) is suggested to be  $\sim 2.5\%$ , so that the ratio of the exchange to reactive channels,  $\gamma$ , is  $<10\%$ . With  $\gamma = 10\%$ ,  $\Delta^{17}O$  is limited to a value of about  $0.1\%$  at  $\delta^{18}O = 20\%$  because its magnitude is determined by both the chemical exchange and transport times. With these reaction rate

coefficients, the  $O(^1D) + N_2O$  reaction cannot be the dominant source of the oxygen anomaly in stratospheric  $N_2O$ , but further laboratory experiments are clearly needed to determine the total branching ratio of the exchange channels. Additional upper bounds on the magnitude of  $\gamma$  may well be obtained from a careful analysis of the experiments of Johnston *et al.* [1995] and Kaiser *et al.* [2002], but we have not yet completed this analysis. It is important to note that we have omitted the doubly substituted reactions since their probability is negligible compared with the effects addressed in the paper. An analysis of  $\gamma$  on the existing data is shown by Röckmann and Kaiser [2005].

### 2. Two-Dimensional Atmospheric Models

[3] To guide further research in this field, we also provide further two-dimensional model results to clarify ambiguities in our paper and provide specific predictions for testing by observations. Figures 1 and 2 present the model results including the  $O(^1D) + N_2O$  exchange reactions with  $\gamma = 50\%$  for the purposes of illustration. It is shown that the magnitude of  $\delta^{18}O$  (Figure 1) can exceed  $15\%$  only at altitudes  $>20$  km, suggesting that either the atmospheric measurements [Cliff *et al.*, 1999; Röckmann *et al.*, 2001] were made in the downwelling part of the Brewer-Dobson circulation or that the troposphere-stratosphere exchange is far more significant than what we have assumed [e.g., Morgan *et al.*, 2004]. Our model results are consistent with those obtained by McLinden *et al.* [2003], which show that the isotopic fractionations of  $N_2O$  are not significant at altitudes below 20 km since the isotopic fractionation of  $N_2O$  is determined primarily by UV photolysis in the stratosphere.

[4] The isotopic anomaly of oxygen in  $N_2O$  under these conditions is shown in Figure 2. The magnitude of the  $\delta^{17}O$  anomaly,  $\Delta^{17}O$ , increases with altitude. At similar altitudes, the values of  $\Delta^{17}O$  at higher latitudes are greater than that at equator. The observed  $\Delta^{17}O \cong 1\%$  and  $\delta^{18}O \sim 18\text{--}20\%$  at 8–12 km are not reproduced in the 2-D model, suggesting that the model may underestimate the strength of stratosphere-troposphere

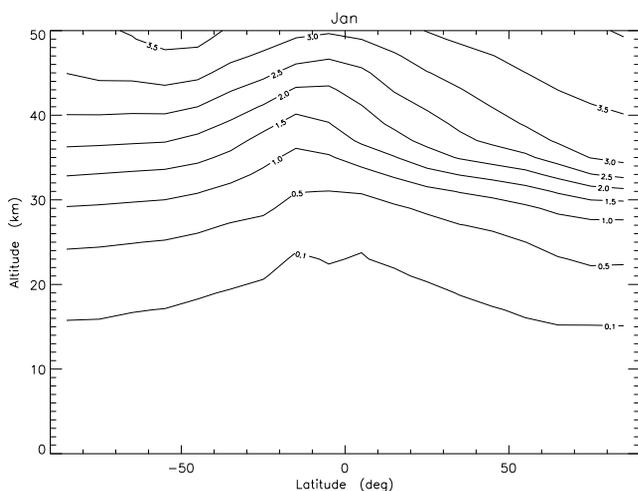


**Figure 1.** Calculated profile of  $\delta^{18}\text{O}$  in January. The values are calculated relative to atmospheric  $\text{O}_2$ .

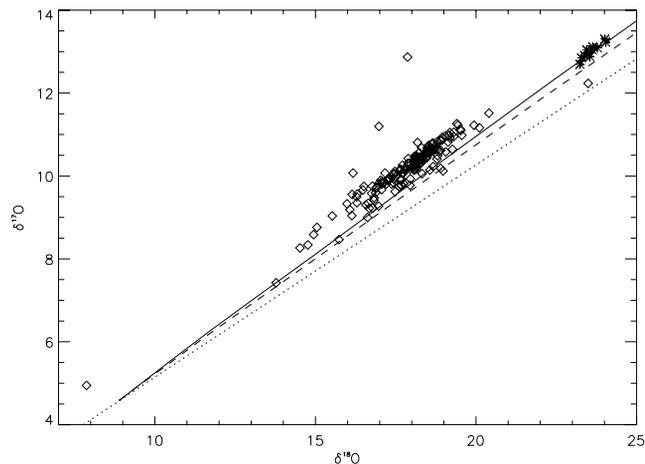
exchange processes. Therefore, we propose that whether an additional source [e.g., Röckmann *et al.*, 2001] exists in the stratosphere or in the troposphere can be tested by measuring the difference of  $\Delta^{17}\text{O}$  between downwelling and upwelling air masses near the tropopause. The photochemical models, including ours, predict that  $\Delta^{17}\text{O}$  is insignificant in upwelling air but that its magnitude is measurable in downwelling air.

[5] The results reported in our paper do not contradict those by Morgan *et al.* [2004]. However, the source strength of 8.9‰ of  $\delta^{18}\text{O}$  in  $\text{N}_2\text{O}$  was not added in the original manuscript [Yung *et al.*, 2004]. The updated plot after incorporating this tropospheric source is shown in Figure 3. We apologize for this oversight. The predicted fractionation is insignificant in the troposphere, and we hope that Figure 1 clarifies any ambiguity in the original paper(s).

[6] In summary, we thank Röckmann and Kaiser [2005] for their insightful and provocative comments. Whether an additional source of  $\text{N}_2\text{O}$  exists in the troposphere or in the stratosphere is critical to resolve the mass-independent isotopic fractionation in atmospheric  $\text{N}_2\text{O}$ .



**Figure 2.** Calculated profile of  $\Delta^{17}\text{O}$  in January.



**Figure 3.** Three-isotope fractionation plot showing the isotopic composition of  $\text{N}_2\text{O}$ . The values are calculated and measured with respect to atmospheric  $\text{O}_2$  and are in units of ‰. The solid (dashed) line shows the impact of the new exchange reactions for  $\gamma = 0.5$  (0.3). For comparison, the typical 0.515 mass-dependent fractionation is given by the dotted line. The diamonds are data from Cliff and Thiemens [1997] and Cliff *et al.* [1999]; the stars are data from Röckmann *et al.* [2001]. A value of 8.9‰ of  $\delta^{18}\text{O}$  in tropospheric  $\text{N}_2\text{O}$  is added. It is important to note that the Cliff *et al.* [1997] measurements are likely due to experimental artifacts [e.g., Röckmann *et al.*, 2001].

## References

- Cliff, S. S., and M. H. Thiemens (1997), The  $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$  ratios in atmospheric nitrous oxide: A mass-independent anomaly, *Science*, **278**, 1774–1776.
- Cliff, S. S., C. A. M. Brenninkmeijer, and M. H. Thiemens (1999), First measurement of the  $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$  ratios in stratospheric nitrous oxide: A mass-independent anomaly, *J. Geophys. Res.*, **104**, 16,171–16,175.
- Johnston, J. C., S. S. Cliff, and M. H. Thiemens (1995), Measurement of multioxygen isotopic ( $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ ) fractionation factors in the stratospheric sink reactions of nitrous-oxide, *J. Geophys. Res.*, **100**, 16,801–16,804.
- Kaiser, J., C. A. M. Brenninkmeijer, and T. Röckmann (2002), Intramolecular  $^{15}\text{N}$  and  $^{18}\text{O}$  fractionation in the reaction of  $\text{N}_2\text{O}$  with  $\text{O}(^1\text{D})$  and its implications for the stratospheric  $\text{N}_2\text{O}$  isotope signature, *J. Geophys. Res.*, **107**(D14), 4214, doi:10.1029/2001JD001506.
- McLinden, C. A., M. J. Prather, and M. S. Johnson (2003), Global modeling of the isotopic analogues of  $\text{N}_2\text{O}$ : Stratospheric distributions, budgets, and the  $^{17}\text{O}$ – $^{18}\text{O}$  mass-independent anomaly, *J. Geophys. Res.*, **108**(D8), 4233, doi:10.1029/2002JD002560.
- Morgan, C. G., M. Allen, M. C. Liang, R. L. Shia, G. A. Blake, and Y. L. Yung (2004), Isotopic fractionation of nitrous oxide in the stratosphere: Comparison between model and observations, *J. Geophys. Res.*, **109**, D04305, doi:10.1029/2003JD003402.
- Nishida, S., K. Takahashi, Y. Matsumi, N. Taniguchi, and S. Hayashida (2004), Formation of  $\text{O}(^3\text{P})$  atoms in the photolysis of  $\text{N}_2\text{O}$  at 193 nm and  $\text{O}(^3\text{P})+\text{N}_2\text{O}$  product channel in the reaction of  $\text{O}(^1\text{D})+\text{N}_2\text{O}$ , *J. Phys. Chem. A*, **108**, 2451–2456.
- Perri, M. J., A. L. Van Wyngarden, K. A. Boering, J. J. Lin, and Y. T. Lee (2003), Dynamics of the  $\text{O}(^1\text{D})+\text{CO}_2$  oxygen isotope exchange reaction, *J. Chem. Phys.*, **119**, 8213–8216.
- Röckmann, T., and J. Kaiser (2005), Comment on “Evidence for O-atom exchange in the  $\text{O}(^1\text{D}) + \text{N}_2\text{O}$  reaction as the source of mass-independent isotopic fractionation in atmospheric  $\text{N}_2\text{O}$ ” by Y. L. Yung *et al.*, *Geophys. Res. Lett.*, **32**, L11807, doi:10.1029/2004GL022149.
- Röckmann, T., J. Kaiser, J. N. Crowley, C. A. M. Brenninkmeijer, and P. J. Crutzen (2001), The origin of the anomalous or “mass-independent” oxygen isotope fractionation in tropospheric  $\text{N}_2\text{O}$ , *Geophys. Res. Lett.*, **28**, 503–506.
- Yung, Y. L., M.-C. Liang, G. A. Blake, R. P. Muller, and C. E. Miller (2004), Evidence for O-atom exchange in the  $\text{O}(^1\text{D}) + \text{N}_2\text{O}$  reaction as

the source of mass-independent isotopic fractionation in atmospheric N<sub>2</sub>O, *Geophys. Res. Lett.*, 31, L19106, doi:10.1029/2004GL020950.

---

G. A. Blake, M.-C. Liang, and Y. L. Yung, Division of Geological and Planetary Sciences, California Institute of Technology, MS150-21, 1200

E. California Boulevard, Pasadena, CA 91125, USA. (mcl@gps.caltech.edu)

C. E. Miller, Atmospheric Chemistry Element, Jet Propulsion Laboratory, Pasadena, CA 91109, USA.

R. P. Muller, Computational Materials and Molecular Biology, Sandia National Laboratories, P.O. Box 5800, MS0196, Albuquerque, NM 87185, USA.