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Evidence for O-atom exchange in the $O(^1D) + N_2O$ reaction as the source of mass-independent isotopic fractionation in atmospheric N_2O

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[1] Recent experiments have shown that in the oxygen isotopic exchange reaction for $O(^1D) + CO_2$ the elastic channel is approximately 50% that of the inelastic channel [*Perri et al.*, 2003]. We propose an analogous oxygen atom exchange reaction for the isoelectronic $O(^1D) + N_2O$ system to explain the mass-independent isotopic fractionation (MIF) in atmospheric N_2O. We apply quantum chemical methods to compute the energetics of the potential energy surfaces on which the $O(^1D) + N_2O$ reaction occurs. Preliminary modeling results indicate that oxygen isotopic exchange via $O(^1D) + N_2O$ can account for the MIF oxygen anomaly if the oxygen atom isotopic exchange rate is 30–50% that of the total rate for the reactive channels. *INDEX TERMS:* 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0341 Atmospheric Composition and Structure: Middle atmosphere—constituent transport and chemistry (3334). **Citation:** Yung, Y. L., M.-C. Liang, G. A. Blake, R. P. Muller, and C. E. Miller (2004), 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.*, *31*, L19106, doi:10.1029/2004GL020950.

1. Introduction

[2] Understanding the isotopic fractionation of atmospheric nitrous oxide (N_2O) is important for constraining the budget for its sources and sinks [see, e.g., *Kim and Craig*, 1993; *Stein and Yung*, 2003]. At present the mass-dependent fractionations have been explained satisfactorily [*Blake et al.*, 2003; *McLinden et al.*, 2003; *Morgan et al.*, 2004; *Liang et al.*, 2004], but there has not been a definitive explanation of the mass-independent fractionation (MIF) of the oxygen isotopic anomaly of atmospheric N_2O.

[3] The N_2O MIF anomaly was discovered by *Cliff and Thiemens* [1997], whose notation we follow. (See *Thiemens et al.* [2001] for an overview of the physical basis and applications of MIF to terrestrial and extraterrestrial environments.) The mass-dependent fractionation for oxygen is given by

$$\delta^{17}O = 0.515\ \delta^{18}O.$$

The oxygen anomaly is defined as the residual from the above equation, or

$$\Delta^{17}O = \delta^{17}O - 0.515\ \delta^{18}O.$$

Cliff and Thiemens [1997] discovered that tropospheric N_2O samples contained $\Delta^{17}O \approx 1‰$. Subsequent measurements confirmed and extended the result into the stratosphere [*Cliff et al.*, 1999; *Röckmann et al.*, 2001]. The latter reference gives $\Delta^{17}O = 1.0 \pm 0.2‰$ at $\delta^{18}O = 20.7 \pm 0.3‰$.

[4] Several mechanisms involving stratospheric N_2O sources have been proposed to explain the observed MIF: $NO_2^* + N_2$ [e.g., *Zellner et al.*, 1992], $O(^1D) + N_2$ [e.g., *Zipf and Prasad*, 1998], $NH_2 + NO_2$ [*Röckmann et al.*, 2001], and others. These processes have been summarized and thoroughly discussed by *McLinden et al.* [2003].

[5] Recently, *Perri et al.* [2003] studied the isotopic exchange reactions for oxygen ($O = {}^{16}O$; $Q = {}^{18}O$) and CO_2:

$$Q(^1D) + CO_2 \rightarrow O(^3P) + COQ$$
$$\rightarrow O(^1D) + COQ.$$

They determined that the inelastic and the elastic channels comprise 68 and 32% of the total exchange cross section, respectively. We argue by analogy that isotopic exchange reactions also occur for the isoelectronic reaction:

$$Q(^1D) + N_2O \rightarrow O + N_2Q, \tag{1}$$

where the product O is the sum of $O(^3P)$ and $O(^1D)$. The chemical reaction between $O(^1D)$ and N_2O is well known to have two product channels [*Sander et al.*, 2000]

$$N_2O + O(^1D) \rightarrow 2NO \tag{2a}$$
$$\rightarrow N_2 + O_2. \tag{2b}$$

The rate coefficients are $k_{2a} = 6.7 \times 10^{-11}$ and $k_{2b} = 4.9 \times 10^{-11}\ cm^3\ s^{-1}$, summing to a total of $k_2 = 1.2 \times 10^{-10}\ cm^3\ s^{-1}$. There have been no reported experimental studies of (1).

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[6] In this paper we use quantum chemical methods to investigate the structure and energetics of the potential energy surfaces for the O(^1D) + N_2O reaction, to assess the possibility of the isotopic exchange reaction. Using the Caltech/JPL two-dimensional (2-D) model, we also carry out a modeling study to estimate the rate coefficient of the isotopic exchange reaction that would be required to explain the observed Δ^{17}O.

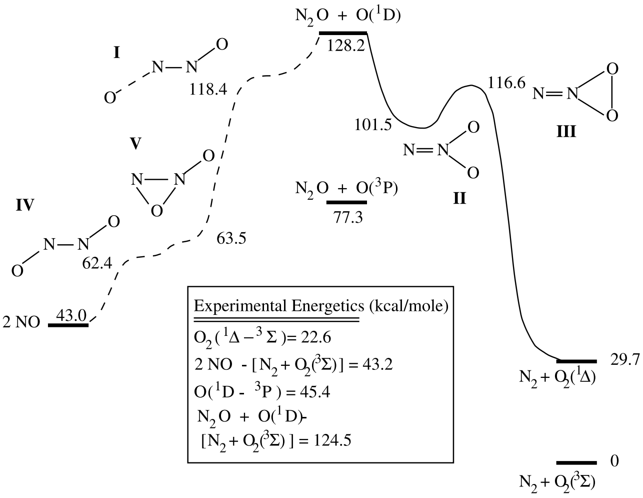
2. Computational Chemistry Calculations

[7] To better understand the potential energy surfaces on which the N_2O + O(^1D) reaction takes place, we have used quantum chemistry methods to investigate the structures and energetics of various intermediates. We have used B3LYP density functional theory (DFT) [*Hohenberg and Kohn*, 1964; *Kohn and Sham*, 1965; *Becke*, 1993] with Dunning's cc-pVTZ(-f) basis set [*Dunning*, 1989], as implemented in the Jaguar program suite (Jaguar 5.5, Schrodinger, LLC, Portland, Oregon, 2003), to obtain optimized structures for all stable species and transition states, including zero-point energy corrections. We then performed single-point coupled-cluster calculations at the SD(T) level (CC-SD(T)) with the Molpro program (version 2002.1) using the optimized DFT structures to obtain more accurate energies for all stable species and transition states.

[8] The results are summarized in Figure 1. Overall, the calculated energetics are within the expected uncertainty limits. For N_2O + O(^1D) $\rightarrow$ N_2 + O_2, $\Delta E_{\text{expt}} = 124.5$, $\Delta E_{\text{calc}} = 128.2$, $\Delta^{\text{calc}-}_{\text{expt}} = 3.7$ kcal/mole, while for (NO + NO)$-$(N_2 + O_2), $\Delta E_{\text{expt}} = 43.2$, $\Delta E_{\text{calc}} = 43.0$, $\Delta^{\text{calc}-}_{\text{expt}} = 0.2$ kcal/mole. Performance is slightly worse for singlet-triplet differences, but still within a factor of 2 of the estimated uncertainty. All intermediates and products are predicted to be exothermic with respect to the reactants and the reaction proceeds with no significant barrier, in agreement with experimental reaction kinetics [*Sander et al.*, 2000]. For O(^1D) attack on the terminal N atom, there is a van der Waals entrance channel that leads to a trans-ONNO intermediate (IV) that lies only ~20 kcal/mole above the 2NO product channel. Lying close in energy to the trans-ONNO structure (IV) is a cyclic intermediate (V) in which one of the oxygen atoms is bound to both N atoms. None of these structures can lead directly to oxygen atom exchange, and no barriers are predicted along this reaction pathway.

[9] For O(^1D) attack on the central N atom, however, there is a C_{2v} intermediate (II) that lies ~27 kcal/mole below the entrance channel. The structure of this intermediate is similar to that the C_{2v} symmetry of CO_3 intermediate thought to promote oxygen atom exchange in the O(^1D) + CO_2 reaction. There is a ~15 kcal/mole barrier that leads directly to the N_2 + O_2 products at the level of theory employed. Although this barrier lies below the entrance channel energy, this barrier can still cause elastic (i.e., non-reactive) scattering. If the C_{2v} intermediate (II) is sufficiently long-lived (of order the vibrational period(s), or a few picoseconds), its symmetry should make oxygen atom exchange possible on the singlet surface. Quenching to the triplet surface may also lead to oxygen atom exchange, but is not calculated here.

[10] The degree to which these processes occur will be sensitive not only to the height and shape of the potential barrier that leads to N_2 + O_2, but also to the coupling of this path on the potential energy surface to other barriers that connect to the cyclic intermediate (V) and thereby to the NO product channel. In principle, the degree of exchange could be calculated by multi-dimensional reactive scattering calculations, but a much finer sampling of the potential energy surface would be required. Such calculations are beyond the scope of this work; however, the calculations presented here illustrate the plausibility of isotopic exchange via (1) and motivate future experimental study of isotopic dependencies in the O(^1D) + N_2O system.



Experimental Energetics (kcal/mole)
$O_2(^1\Delta - ^3\Sigma) = 22.6$
2 NO - [N_2 + $O_2(^3\Sigma)$] = 43.2
O(^{1}D - ^{3}P) = 45.4
N_2O + O(^{1}D)- [N_2 + $O_2(^3\Sigma)$] = 124.5

Figure 1. A summary of the calculations for the O(^1D) + N_2O singlet reaction surface. All energies are in kcal/mol, and are the results of CC-SD(T) calculations with zero-point energy corrections from B3LYP density functional theory. Transition states for the 2NO product channel are connect by the dotted curve as a guide to the eye, the N_2 + O_2 product channel is highlighted by the solid curve. Experimental values for the reactant and product energetics are summarized in the table at center.

3. Photochemical Modeling Results and Discussion

[11] The Caltech/JPL 2-D model for simulating the distribution of N_2O and its isotopologues and isotopomers has been described elsewhere [*Morgan et al.*, 2004]. The model has 18 latitudes from pole to pole, and 40 layers from 1000 to 0.01 mbar. The wind fields are derived from the reanalysis product from the National Center for Environmental Prediction and Department of Energy [*Jiang et al.*, 2004]. Four new reactions are added to the model. They are reaction (1) and

$$\mathrm{O}\left(^1D\right) + \mathrm{N_2Q} \rightarrow \mathrm{Q} + \mathrm{N_2O} \tag{3}$$

$$\mathrm{P}\left(^1D\right) + \mathrm{N_2O} \rightarrow \mathrm{O} + \mathrm{N_2P} \tag{4}$$

$$\mathrm{O}\left(^1D\right) + \mathrm{N_2P} \rightarrow \mathrm{P} + \mathrm{N_2O}, \tag{5}$$

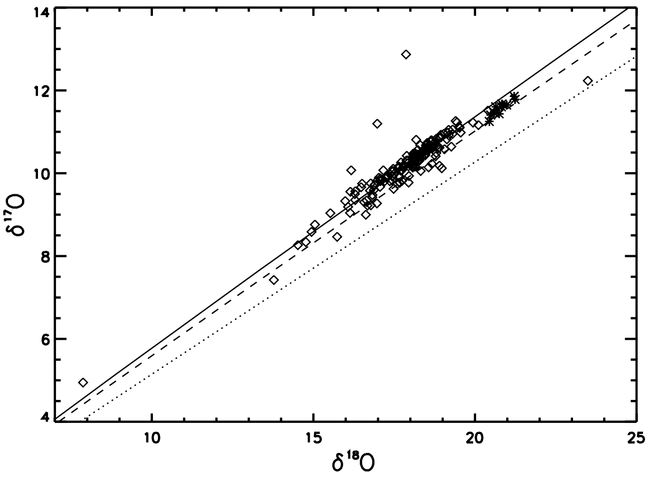


Figure 2. Two-isotope fractionation plot showing the isotopic composition of N_2O. The values are calculated and measured with respect to air O_2 and are in units of ‰. The solid (dashed) line shows the impact of the new exchange reactions for $\gamma = 0.5$ (0.3). For comparison, the typical 0.515 mass-dependent 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].

where $P = {}^{17}O$. These four reactions describe the forward and reverse exchange for ^{18}O and ^{17}O with $N_2^{16}O$. For lack of information, we assume $k_1 = k_3 = k_4 = k_5 = \gamma k_2$, where γ is an unknown constant.

[12] One may ask why the addition of these four reactions could produce an MIF in N_2O. The reason is simple. Suppose N_2O were in photochemical equilibrium with $O(^1D)$, then the reactions (1), (3), (4) and (5) imply

$$N_2Q/N_2O = Q(^1D)/O(^1D) \tag{6}$$

$$N_2P/N_2O = P(^1D)/O(^1D). \tag{7}$$

In other words, N_2O equilibrates isotopically with $O(^1D)$. Since $O(^1D)$ is known to have MIF, its MIF is transferred to N_2O, much as in the case of CO_2 [*Thiemens et al.*, 1991; *Yung et al.*, 1991; *Wen and Thiemens*, 1993; *Yung et al.*, 1997]. Mixing in the atmosphere tends to dilute the MIF, and the net effect is much less than that given by the isotopic equilibrium. Because $\delta Q \approx \delta P \approx 100‰$, the induced MIF may still be non-trivial even after extensive dilution by mixing.

[13] The results of our model for the cases $\gamma = 0.3$, 0.5 and $\delta Q = \delta P = 100‰$ are summarized in Figure 2. The dotted line is the baseline case, i.e., no isotopic exchange ($\gamma = 0$). The solid (dashed) line shows the impact of the new exchange reactions for $\gamma = 0.5$ (0.3). These values of γ are consistent with the experimentally determined isotopic exchange reaction for $O(^1D) + CO_2$. Figure 2 illustrates that isotopic exchange reactions in the range $0.3 < \gamma < 0.5$ are of the correct order of magnitude to explain the bulk of the 2-isotope observations for atmospheric N_2O.

[14] In summary, we have demonstrated the feasibility of transferring oxygen MIF enrichment from O_3 to N_2O if the exchange channel were as large as 30–50% of the reactive channels. Even a smaller isotopic exchange rate coefficient would still account for part of the observed MIF, leaving the rest to be explained by other mechanisms. Experimental verification of our proposal would yield interesting new insight into the atmospheric chemistry of N_2O.

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