Rapid photochemical equilibration of isotope bond ordering in \( \text{O}_2 \)

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Abstract

The abundances of \( ^{18}\text{O}^{18}\text{O} \) and \( ^{17}\text{O}^{18}\text{O} \) in the atmosphere were recently found to be enriched relative to the stochastic distribution of isotopes in \( \text{O}_2 \). The enrichment is believed to arise from \( \text{O}^3\text{P} + \text{O}_2 \) isotope exchange reactions, which reorder the isotopes in \( \text{O}_2 \) to a distribution that favors bonds between heavy isotopes. Theoretical predictions and laboratory experiments suggest that the reordered distribution of isotopes should reflect internal isotopic equilibrium, but a laboratory test of this hypothesis for the complete \( \text{O}_2 \) isotopologue system has not yet been realized. Here we use a simple photochemical experiment that reorders the isotopes in \( \text{O}_2 \) at temperatures between 200 K and 350 K. Using simultaneous measurements of five \( \text{O}_2 \) isotopologues, we show that \( \text{O}^3\text{P} + \text{O}_2 \) reorders the isotopes in \( \text{O}_2 \) to isotopic equilibrium. Furthermore, we use this scheme to calibrate measurements of isotopic ordering in samples of \( \text{O}_2 \), obtaining \( \Delta_{36} \) and \( \Delta_{35} \) values within \( \pm 0.1\% \). Measurements of atmospheric \( \text{O}_2 \) sampled at the University of California, Los Angeles, from 2012 to 2014 have mean values of \( \Delta_{36} = 1.97 \pm 0.07\% \) and \( \Delta_{35} = 1.0 \pm 0.1\% \) (2SE; \( n = 23 \)), with no detectable long-term trend. These measurements are consistent with values for air reported earlier, but with a threefold to fourfold improvement in precision. Together, the experiments and observations support the case that isotopic ordering in tropospheric \( \text{O}_2 \) is altered by \( \text{O}^3\text{P} \) reactions, and they also suggest that tropospheric \( \Delta_{36} \) and \( \Delta_{35} \) values do not reflect complete isotopic equilibration in the troposphere. Isotopic ordering in atmospheric \( \text{O}_2 \) likely reflects the decadal-scale balance of stratospheric and tropospheric air masses modulated by variations in tropospheric photochemistry and convection.

1. Introduction

Molecular oxygen is the most important biogeochemical gas in the atmosphere. It holds a unique record of biological, hydrological, and photochemical signatures within its isotopic composition. This record provides constraints on the coevolution of the biosphere, hydrosphere, and atmosphere on time scales relevant to both abrupt and protracted climate change [Bender et al., 1994; Luz et al., 1999; Blunier et al., 2002; Landais et al., 2007; Severinghaus et al., 2009]. Until recently, however, only the bulk isotopic composition of \( \text{O}_2 \) (i.e., its \( ^{18}\text{O}^{16}\text{O} \) and \( ^{17}\text{O}^{16}\text{O} \) ratios) had been studied. In nature, this composition varies primarily in response to biological oxygen cycling, although the influence of stratospheric photochemistry can also be detected [Guy et al., 1989, 1993; Luz et al., 1999; Angert et al., 2003; Young et al., 2014].

The recent addition of \( ^{18}\text{O}^{16}\text{O} \) and \( ^{17}\text{O}^{16}\text{O} \) to isotopic analyses of \( \text{O}_2 \) revealed new information recorded in atmospheric \( \text{O}_2 \) [Yeung et al., 2012]. The simultaneous measurements of five \( \text{O}_2 \) isotopologues (\( ^{16}\text{O}^{16}\text{O}, ^{16}\text{O}^{17}\text{O}, ^{16}\text{O}^{18}\text{O}, ^{17}\text{O}^{18}\text{O}, \) and \( ^{18}\text{O}^{18}\text{O} \) O) showed that a signature of \( ^{16}\text{O}, ^{17}\text{O}, \) and \( ^{18}\text{O} \) ordering in \( \text{O}_2 \) was also present and controlled largely by the photochemistry of the odd oxygen system (i.e., \( \text{O}_3 + \text{O} \)). This isotopic ordering in atmospheric \( \text{O}_2 \) was found to be nonstochastic, with \( ^{18}\text{O}^{16}\text{O} \) and \( ^{17}\text{O}^{16}\text{O} \) enriched relative to a random distribution of isotopes (i.e., \( \Delta_{36} > 0 \) and \( \Delta_{35} > 0 \), respectively). To explain this observation, Yeung et al. [2012] hypothesized that \( \text{O}^3\text{P} + \text{O}_2 \) isotope exchange reactions reorder the isotopes in \( \text{O}_2 \) toward an isotopic equilibrium that depends on temperature: At low temperatures, the \( ^{18}\text{O}^{16}\text{O} \) and \( ^{17}\text{O}^{16}\text{O} \) enrichments should be relatively high, whereas at higher temperatures, the enrichments are expected to be low. Moreover, because temperatures are not uniform in the atmosphere, the dynamic balance between tropospheric and stratospheric processes was expected to have a strong influence on atmospheric \( \Delta_{36} \) and \( \Delta_{35} \) values. However, a definitive confirmation of the kinetics of isotopic reordering and its effects on \( \Delta_{36} \) and \( \Delta_{35} \) values at different temperatures was lacking.

In this study, we use photochemical experiments to show that isotope exchange reactions between \( \text{O}^3\text{P} \) (i.e., oxygen atoms in their ground electronic state) and \( \text{O}_2 \) can explain both the kinetics of isotopic ordering and
the steady state \( \Delta_{36} \) and \( \Delta_{35} \) values in \( \text{O}_2 \) upon irradiation with UV light. We investigated the time evolution of \( \Delta_{36} \) and \( \Delta_{35} \) values at 300 K and compared the results to predictions from theoretical calculations [Kaye and Strobel, 1983; Hathorn and Marcus, 2000; Fleurat-Lessard et al., 2003]. We also compared \( \Delta_{36} \) and \( \Delta_{35} \) values at steady state to the values predicted at isotope exchange equilibrium [Wang et al., 2004]. Finally, we used these experiments to calibrate and interpret 14 months of \( \Delta_{36} \) and \( \Delta_{35} \) measurements in air at the University of California, Los Angeles (UCLA). These results constitute a high-precision calibration method for \( \Delta_{36} \) and \( \Delta_{35} \) values (±0.1‰) that can be replicated independently in other laboratories for a wide variety of chemical and biogeochemical applications. They also validate the longstanding hypothesis that \( \text{O}_2 \) quickly reaches internal isotopic equilibrium in the ozone photochemical system [Kaye and Strobel, 1983; Anderson et al., 1997; Hathorn and Marcus, 2000; Fleurat-Lessard et al., 2003].

2. Isotopic Ordering: Definitions

Quantities of \( ^{18}\text{O}^{16}\text{O} \) and \( ^{17}\text{O}^{16}\text{O} \) (i.e., mass-36 and mass-35 \( \text{O}_2 \)) are reported relative to the stochastic distribution of isotopes in \( \text{O}_2 \). Using the notation described in Yeung et al. [2012], where \( ^{17}R \) indicates molecular ratios, we characterize proportional \( ^{18}\text{O}^{16}\text{O} \) abundances using

\[
\Delta_{36} = \left( \frac{R_{\text{measured}}}{R_{\text{stochastic}}} - 1 \right) .
\]

where

\[
R_{\text{measured}} = \left( \frac{[^{16}\text{O}]^{[16}\text{O}}{[^{12}\text{O}]^{[12}\text{O}}} \right) \quad \text{and}\quad R_{\text{stochastic}} = \left( \frac{[^{18}\text{O}]^{[16}\text{O}}{[^{16}\text{O}]^{[16}\text{O}}} \right) = \left( R^{18}_{\text{O}} \right)^2 .
\]

(2)

Similar \( \Delta_n \) terminology describes proportional abundances of \( ^{17}\text{O}^{18}\text{O} \); however, an additional factor of 2 is present in the stochastic distribution, i.e.,

\[
R_{\text{measured}} = \left( \frac{[^{35}\text{O}]^{[32}\text{O}}{[^{32}\text{O}]^{[32}\text{O}}} \right) \quad \text{and}\quad R_{\text{stochastic}} = \left( \frac{2[^{17}\text{O}]^{[16}\text{O}}{[^{16}\text{O}]^{[16}\text{O}}} \right) = 2 \times 17^{18}R_{\text{O}^{18}}.
\]

(3)

because \( ^{17}\text{O}^{18}\text{O} \) has two symmetrically equivalent isotopomers. Enrichments and deficits in \( \Delta_n \) notation are reported in per mil (‰): \( \Delta_{36} \) and \( \Delta_{35} \) values equal to zero represent a random distribution of isotopes, whereas a positive or negative \( \Delta_n \) value represents an overabundance or under-abundance of \( ^{18}\text{O}^{16}\text{O} \) or \( ^{17}\text{O}^{18}\text{O} \), respectively, relative to the stochastic distribution defined in equations (2) and (3). These values represent isotopic ordering when they change as a result of bond alteration, such as during isotope exchange reactions.

We note that equilibrium in the context of isotopic ordering references an equilibrium distribution of isotopes among molecules comprising a single molecular species. Isotopic equilibrium between multiple species (e.g., between \( \text{O}_2 \) and \( \text{O}_3 \)) depends on the partitioning of isotopes among all relevant isotopologues, which can be significantly more complex. In this paper, we investigate only isotopic ordering in \( \text{O}_2 \), which can be established independently from, and on different time scales than, the bulk isotopic partitioning that occurs between the oxygen-containing molecular species in a gas-phase photochemical system. The reader is directed to the literature on the isotope effects of \( \text{O}_3 \) formation for discussions of photochemical equilibrium between \( \text{O}_2 \) and \( \text{O}_3 \) [Janssen, 2005].

3. Laboratory Experiments

3.1. Experimental Apparatus

Photochemical experiments were carried out in a 1000 mL round-bottom Pyrex flask (radius = 6.2 cm; see Figure 1). It had a single vacuum valve attached via 13 cm × 9 mm ID tube and a quartz-and-Pyrex transition tube inset (9 cm × 11 mm ID, 13 mm OD inside the bulb). The length of the quartz tubing inside the bulb was 7.6 cm; a 12 cm glass extension to the exterior was sealed against the quartz-to-Pyrex transition and to the bulb. Ultraviolet light was generated with a Pen-Ray mercury line source (UVP model 3SC-9) inserted through the open extension to illuminate the bulb through the short length of quartz (7.6 cm) inside. A flow of nitrogen was utilized to flush out potential UV absorbers between the lamp and the quartz. To vary the reaction temperature, the entire apparatus was submerged in a large dewar filled with either water or liquid N\(_2\)-cooled ethanol at different temperatures.
Thermocouples (Type K) were used to monitor the temperature of the liquid bath and the quartz finger. Bath temperatures were maintained to within ± 2°C.

This geometrically and optically simple apparatus allows one to calculate the reaction conditions. For example, the photon flux into the bulb can be calculated based on the manufacturer-specified irradiances at 254 nm (5400 μW cm⁻² at 1.9 cm) and 185 nm (3% of flux at 254 nm), the optical transmission through the quartz (80% at 254 nm, 30% at 185 nm), and the geometry of the quartz portion of the tube. The typical photon flux at the surface of the quartz finger was 6 × 10¹⁶ photons cm⁻² s⁻¹, and the volume-weighed mean number density in the bulb is calculated to have been 2.3 × 10¹⁵ photons cm⁻³ s⁻¹ (see section 3.2.1).

Elevated temperatures were observed inside the finger during lamp operation, necessitating a calculated adjustment to gas temperatures above the bath temperature. The fixed surface area of the finger (39 cm²) and bulb (487 cm²) allowed us to calculate the mean internal temperature based on the Stefan-Boltzmann law. For example, when the bulb was immersed in water at 298 K, the temperature of the finger was typically 343 K at steady state after the lamp had warmed up. We calculated a mean gas temperature of $T_{\text{gas}} = 302 \text{ K}$ using the relationship

$$T_{\text{gas}}^4 = \left(\frac{39}{526}\right) \times T_{\text{finger}}^4 + \left(\frac{487}{526}\right) \times T_{\text{bath}}^4.$$  

This temperature, which was 4 K higher than the immersion bath temperature, was used to calculate the equilibrium temperature for isotopic ordering inside the bulb.

Samples of O₂ were analyzed immediately following photolysis because both thermal and photolytic decomposition of O₃ can reorder the isotopes in the O₂ sample. Indeed, an O₂ sample that was initially equilibrated photochemically at 278 K was reordered to room temperature isotopic equilibrium after being stored for several months in room light and at room temperature (see section 3.4). Glass and quartz have very low reactivity, however, so the presence of O₃ likely catalyzed the isotopic reordering in this instance. Long-term storage in glass and quartz vessels may not necessarily equilibrate the distribution of isotopes in O₂ without such a catalyst.

### 3.2. Photochemical Model
#### 3.2.1. Mercury Lamp Irradiance

The 254 nm and 185 nm photon fluxes derived in the previous section were converted to mean photon number density for input into a photochemical model. The simple geometry of the apparatus enabled this calculation: The quartz portion of the interior finger was treated as a cylinder (7 cm × 13 mm diameter) plus a hemispherical end ($r = 6.5$ mm). The photon flux entering the evacuated part of the bulb through the quartz finger was then calculated using the view factor method [Modest, 2013]:

$$\text{Power} = \frac{E_{\text{UV}}}{2\pi r l_{\text{tot}}} F_{\text{total}},$$  

where $E_{\text{UV}}$ is the power output of the lamp in microwatts, $r$ is the lamp's radius (4.75 mm), $l_{\text{tot}}$ is the total length of the cylinder (7 cm; the hemispheric end was treated separately), and $F_{\text{total}}$ is the fraction of the...
lamp’s power output incident on a given area dA in free space (i.e., its view factor). This view factor was computed by splitting it into two sections for any given position in between the two ends of the lamp,

$$ F_{\text{total}} = F_1 + F_2, $$

where $l_1$ and $l_2$ represent the distances from the ends of the lamp for any point in space projected onto the cylindrical lamp. The view factor for each of these segments is computed as a function of $l$ and $d$ (the distance from the lamp) according to the following equation:

$$ F_l = \frac{L}{\pi H} \left[ \tan^{-1}\left( \frac{L}{\sqrt{H^2 - l^2}} \right) - \tan^{-1}(M) + \frac{X}{\sqrt{XY}} \tan^{-1}\left( \frac{X}{Y} \right) \right], $$

where $L$, $H$, $X$, $Y$, and $M$ are defined as follows:

$$ L = \frac{l}{r}, $$

$$ H = \frac{d}{r}, $$

$$ X = (1 + H)^2 + L^2, $$

$$ Y = (1 - H)^2 + L^2, $$

$$ M = \frac{H - 1}{H + 1}. $$

This method of calculation agrees well with radiometric measurements, both axially and radially, whereas a simple inverse square dependence overestimates the incident power at distances less than 10 cm [Kowalski and Bahnflath, 2000]. The UV flux from the hemispheric end to the quartz finger was then added to the calculated flux from the cylinder using the inverse-square law. The walls of the Pyrex bulb were treated as perfect absorbers of UV light.

A schematic of the reaction bulb, with a contour plot of the modeled irradiance within the bulb, is shown in Figure 1. The irradiance decreased with distance from the quartz finger, from 15 to 20 mW at the surface to nearly zero at the wall. It reproduced the manufacturer-specified irradiance of 3400 µW at 1.9 cm using an initial UV flux of 5600 µW. To calculate the photon number density, the irradiance was integrated volumetrically within the bulb volume. The resulting average photon number density inside the bulb was $2.3 \times 10^{15}$ photons cm$^{-3}$ s$^{-1}$ at 254 nm ($2.9 \times 10^{15}$ photons cm$^{-3}$ s$^{-1}$ with 80% transmission) and $2.6 \times 10^{13}$ photons cm$^{-3}$ s$^{-1}$ at 185 nm (3% of the flux at 254 nm with 30% transmission through quartz). These values are similar to those calculated for other experiments involving a mercury line source [Wiegel et al., 2013], and they were used in the photochemical model without further adjustment.

### 3.2.2. Chemistry

To simulate the kinetics of the photochemical experiments, a reaction network for the O$_2$/O$_3$ photochemical system was built in KINTECUS [Ianni, 2003] using literature reaction rate coefficients and photolysis cross sections [Yoshino et al., 1992; Sander et al., 2011; Wiegel et al., 2013]. Isotope exchange, ozone formation, and excited-state oxygen photochemistry, i.e., that involving O($^1D$), O$_2$($^1\Sigma$), and O$_2$($^1\Pi$), were included to model concentrations of O($^3P$) accurately (see Table 1). The relative chemical simplicity of the reaction system also allowed a thorough treatment of O$_2$ and O$_3$ isotopologues. In total, the model contained 321 reactions (see supporting information). A brief description of its major features follows.

The reactions with the most significant effects on $\Delta_{36}$ and $\Delta_{35}$ values are the isotope exchange reactions. Temperature-dependent rates of oxygen isotope exchange for $^{16}$O($^3P$) + $^{18}$O$^{16}$O and $^{18}$O($^3P$) + $^{18}$O$^{18}$O were taken from the combined theoretical-experimental study by Fleurat-Lessard et al. [2003] ($3.4 \times 10^{-12}$ cm$^3$ s$^{-1}$ and $2.7 \times 10^{-12}$ cm$^3$ s$^{-1}$, respectively, at 300 K). These rate coefficients were consistent with results from other laboratory experiments [Anderson et al., 1985b; Wiegell et al., 1997]. The rates of O($^3P$) + O$_2$ isotope exchange involving other isotopologues have not been directly predicted or measured, but the principle of microscopic reversibility allows one to derive relative rate coefficients based on equilibrium constants of each reaction. Relative O($^3P$) + O$_2$ isotope exchange rate coefficients were therefore calculated using the reduced partition function ratios of the O$_2$ isotopologues involved in each reaction (see Table 2), similar to the method used in previous calculations [Kaye and Strobel, 1983; Hathorn and Marcus, 2000]. These relative rates are expected to yield the equilibrium isotopologue distributions for $^{16}$O$^{18}$O ($\Delta_{36}$) calculated in Wang et al. [2004]. An additional seven rate coefficients
Table 1. Reactions Families in Photochemistry Model

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient at 300 K</th>
<th>References and Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ + hν(185 nm) → O(3P) + O(3P)</td>
<td>1.0 × 10⁻⁷ cm³ s⁻¹</td>
<td>Sander et al. [2011]</td>
</tr>
<tr>
<td>O₂ + hν (254 nm) → O₂(1Δ) + O(1D) → O₂ + O(3P)</td>
<td>9.9 × 10⁻⁸ cm³ s⁻¹</td>
<td>Sander et al. [2011]</td>
</tr>
<tr>
<td>Q → O(3P) → O₂ + O(3P)</td>
<td>3.0 × 10⁻¹⁰ cm³ s⁻¹</td>
<td>Isotope exchange coefficient; see supporting information for isotopologue-specific rate coefficients. For ¹⁶O¹⁸O: see supporting information for isotopologue-specific rate coefficients from Mauersberger et al. [1999], Schinke et al. [2006], and Gao and Marcus [2007].</td>
</tr>
<tr>
<td>2O₂ + O(3P) → O₂ + O₂</td>
<td>6.0 × 10⁻³⁴ cm⁶ s⁻¹</td>
<td>Sander et al. [2011]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient at 300 K</th>
<th>References and Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ + O²⁻(3P) → 2O₂</td>
<td>8.3 × 10⁻¹⁵ cm³ s⁻¹</td>
<td>Sander et al. [2011]</td>
</tr>
<tr>
<td>O₂ + O(3D) → 2O₂</td>
<td>1.2 × 10⁻¹⁰ cm³ s⁻¹</td>
<td>Sander et al. [2011]</td>
</tr>
<tr>
<td>O₂ + O(3P) → O₂ + O(3P)</td>
<td>1.2 × 10⁻¹⁰ cm³ s⁻¹</td>
<td>Sander et al. [2011]</td>
</tr>
<tr>
<td>O₂ + O²⁻(3P) → O₂ + O⁺(3P)</td>
<td>0.2 × [4.0 × 10⁻¹⁰ cm³ s⁻¹</td>
<td>Sander et al. [2011]</td>
</tr>
<tr>
<td>O₂ + O²⁻(3P) → O₂ + O⁺(3P)</td>
<td>0.8 × [4.0 × 10⁻¹⁰ cm³ s⁻¹]</td>
<td>Sander et al. [2011]</td>
</tr>
<tr>
<td>O₂(1Δ) + O₂ → 2O₂</td>
<td>1.7 × 10⁻¹⁸ cm³ s⁻¹</td>
<td>Sander et al. [2011]</td>
</tr>
<tr>
<td>O₂(1Δ) + O₂ → 2O₂(1Δ)</td>
<td>4.0 × 10⁻¹⁵ cm³ s⁻¹</td>
<td>Sander et al. [2011]</td>
</tr>
<tr>
<td>O₂(1Σ) + O₂ → 2O₂(1Δ) + O₂</td>
<td>4.0 × 10⁻¹⁷ cm³ s⁻¹</td>
<td>Sander et al. [2011]</td>
</tr>
<tr>
<td>O₂(1Σ) + O₂ → 2O₂(1Δ) + O₂</td>
<td>0.3 × [2.2 × 10⁻¹¹ cm³ s⁻¹]</td>
<td>Sander et al. [2011]</td>
</tr>
<tr>
<td>O₂(1Σ) + O₂ → 2O₂(1Δ) + O₂</td>
<td>0.7 × [2.2 × 10⁻¹¹ cm³ s⁻¹]</td>
<td>Sander et al. [2011]</td>
</tr>
<tr>
<td>O₂(1Σ) + O(3P) → O₂(2Δ) + O(3P)</td>
<td>8.0 × 10⁻¹⁴ cm³ s⁻¹</td>
<td>Sander et al. [2011]</td>
</tr>
</tbody>
</table>

* A list of all isotopologue-specific reaction rates used in the model can be found in the supporting information. Here Q represents any stable isotope of oxygen.

are required to describe the remaining 14 reactions involving ¹⁷O. For those reactions, we used nominal rate coefficients of 1.5 × 10⁻¹² cm³ s⁻¹ for each product channel [e.g., ¹⁷O(²P) + ¹⁶O¹⁰O → ¹⁶O²P + ¹⁷O¹⁰O]. For reactions with O₂ reactants that were homonuclear [e.g., ¹⁸O(²P) + ¹⁷O¹⁰O → ¹⁷O²P + ¹⁸O¹⁰O], the two identical product channels were summed to 3 × 10⁻¹² cm³ s⁻¹. While the use of these nominal rate coefficients was a necessary approximation to model the kinetics of Δ₃₅O variations in them had a negligible effect on the modeled Δ₃₆O and Δ₃₅O kinetics when the coefficients were doubled or halved. A full quantum dynamical or transition state theory calculation of these rate coefficients is beyond the scope of this study, which focuses on quantities that depend mainly on the relative rates.

Isotopologue-specific O₃ formation rate coefficients, where available, were taken from Mauersberger et al. [1999]. The rate coefficients for the ¹⁸O¹⁷O¹⁸O-forming channels were derived from theoretical predictions [Schinke et al., 2006; Gao and Marcus, 2007] because they were not measured by Mauersberger et al. [1999]. For simplicity, position-specific isotopic substitutions within O₃ molecules were not explicitly represented; no distinction was made between ¹⁸O¹⁶O¹⁶O and ¹⁶O¹⁸O¹⁶O. While this treatment has important consequences for the isotopic enrichments in O₃, our experiments were conducted at low pressures (3–10 mbar), where little O₃ is formed. At these pressures, the mass balance favors O₂ by a factor of 10⁴, and the rate of isotopic exchange is 10⁶ times faster than that of O₃ formation. Furthermore, the production of molecular oxygen through other channels, e.g., O₃ photolysis, O₂(1Δ) + O₃, and O₁(¹D) + O₃, occurs at less than 5% of the rate of O₂(²P) + O₃ isotope exchange. The time evolution of Δ₃₆O was therefore controlled by the O₂(²P) concentration and the rates of O₂(²P) + O₂ isotope exchange.

Table 2. Isotope Exchange Equilibrium Constants at 300 K Used in Photochemistry Model

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Kₑq,300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹⁶O₂(²P) + ¹⁷O¹⁷O → ¹⁶O²P + ¹⁸O¹⁰O</td>
<td>1.9180</td>
</tr>
<tr>
<td>¹⁶O₂(²P) + ¹⁸O¹⁰O → ¹⁶O²P + ¹⁶O¹⁸O</td>
<td>1.8463</td>
</tr>
<tr>
<td>¹⁷O₂(²P) + ¹⁶O¹⁰O → ¹⁷O²P + ¹⁶O¹⁰O</td>
<td>2.0846</td>
</tr>
<tr>
<td>¹⁷O₂(²P) + ¹⁸O¹⁰O → ¹⁷O²P + ¹⁷O¹⁰O</td>
<td>1.9259</td>
</tr>
<tr>
<td>¹⁸O₂(²P) + ¹⁶O¹⁰O → ¹⁸O²P + ¹⁶O¹⁰O</td>
<td>2.1633</td>
</tr>
<tr>
<td>¹⁸O₂(²P) + ¹⁷O¹⁰O → ¹⁸O²P + ¹⁷O¹⁰O</td>
<td>2.0762</td>
</tr>
<tr>
<td>¹⁶O₂(²P) + ¹⁷O¹⁰O → ¹⁶O²P + ¹⁷O¹⁰O</td>
<td>0.9586</td>
</tr>
<tr>
<td>¹⁶O₂(²P) + ¹⁸O¹⁰O → ¹⁶O²P + ¹⁸O¹⁰O</td>
<td>0.9238</td>
</tr>
<tr>
<td>¹⁷O₂(²P) + ¹⁷O¹⁰O → ¹⁷O²P + ¹⁷O¹⁰O</td>
<td>0.9637</td>
</tr>
</tbody>
</table>

The experiment was treated as isothermal for two reasons. First, we calculated that heating of the gas in the bulb due to light absorption would be negligible, even in the absence of a thermal bath: The optical depth was always < 10⁻³ cm⁻¹ for O₃ and O₂, yielding < 10 μW of light absorbed. Second, nearly all isotope exchange reactions should occur thermally because hyperthermal collisions, which would raise the
effective reaction temperature, are rendered insignificant by the rapid recycling of \( \text{O}(^{3}P) \) of all the \( \text{O}(^{3}P) + \text{O}_{2} \) collisions leading to isotope exchange events, those coming from nascent hyperthermal collisions are vanishingly few in number.

The low pressures in the reaction bulb also increase the importance of wall effects, but we expect gas phase isotope exchange reactions to dominate the isotopic ordering signal during the relatively short (\(<1\) h) experiments described here. The mean free path of \( \text{O}(^{3}P) \) is \(< 225 \mu\text{m} \) at \( 300 \text{K} \) \((Z = 8 \times 10^{3} \text{s}^{-1})\), and approximately one out of thirty \( \text{O}(^{3}P) + \text{O}_{2} \) collisions results in isotope exchange. In addition, previous studies suggest that the \( \text{O} + \text{O}_{2} \) recombination efficiency on Pyrex is \(< 1\% \) above \( 100 \text{K} \), with quenching of excited \( \text{O}_{2}^{*} \) on walls being orders of magnitude less likely [Macko et al., 2004; Janssen and Tuazon, 2010]. Nonetheless, both of these effects would increase the effective rate of \( \text{O}_{3} \) formation, leading to enhanced photolytic generation of atomic oxygen. Recombination of two oxygen atoms to form \( \text{O}_{2} \) is expected to be negligible because of low atomic oxygen concentrations. In summary, the net effect of wall-assisted recombination reactions should be negligible; however, they could increase the rate of gas phase isotopic reordering by increasing \( \text{O}(^{3}P) \) concentrations slightly.

### 3.3. Analytical Methods

Our analytical procedures were modified slightly from those described in Yeung et al. [2012]. To analyze the isotopologues of \( \text{O}_{2} \), samples containing 150–200 \( \mu\text{mol} \) of \( \text{O}_{2} \) were passed through a gas chromatograph purification system (GC; molecular sieve 5A column, 3 m \times 1/8 inch OD) at \(-80°C \) to remove \( \text{N}_{2} \) and Ar. The ultrahigh-purity helium carrier gas used for this system (99.9995%) was further purified by passing it through a silica gel column (6 feet \times 1/8 inch OD) and a molecular sieve 5A U-trap, both of which were immersed in liquid nitrogen. After the GC separation, the purified \( \text{O}_{2} \) was adsorbed onto a molecular sieve adsorbent at \(-196°C \), transferred to an isotope ratio mass spectrometer (IRMS; ThermoFinnigan MAT 253), and then purified for its isotopic composition against a working reference gas \((m/z = 32–36)\). Standard gases were then measured and measured over a range of Ar concentrations to obtain ion-correction relationships for the \( ^{36}\text{Ar}^{18}\text{O}^{16}\text{O} \) isobaric interference. The residual Ar content of the sample was measured by peak-hopping to obtain the voltage \((\text{i.e., ion current})\) compared with that of the standard \((V_{40.5A}/V_{40.5T})\) at three separate times during the 5 h analysis time \((90–120\) sample standard comparison cycles with \(10\) s per individual integration and a \(25\) s preintegration delay). The inferred \( ^{36}\text{Ar} \) concentration of the sample was then used to correct the measured \( m/z = 36 \) ion beam for interfering \( ^{36}\text{Ar} \) about \(7–18\) mV out of \(400\) mV total. The IRMS procedures are described in detail in Yeung et al. [2012] and in Appendix A. This analytical method yields \( \Delta_{36} \) and \( \Delta_{35} \) values with a precision of \(1\sigma \approx \pm 0.1\‰\) and \(\pm 0.2\‰\), respectively, at a rate of two analyses \((\text{one sample and one standard})\) per day. Precision for \( \delta^{18}\text{O} \) and \( \Delta^{17}\text{O} \) with this method are \(\pm 0.04\‰\) and \(5\) ppm, respectively [Yeung et al., 2014].

The measurements were standardized against gases generated using the reversible decomposition of \( \text{BaO}_{2} \) powder at \(800°C \):

\[
2\text{BaO}_{2}(s) \rightarrow 2\text{BaO}(s) + \text{O}_{2}(g).
\]  

The resulting \( \text{O}_{2} \) gas is at high-temperature isotopic equilibrium \((\Delta_{36} = 0.03\‰\) and \( \Delta_{35} = 0.02\‰\) at \(800°C \)) [Wang et al., 2004], thus resembling the stochastic distribution used to define \( \Delta_{n} \) values. The \( \text{O}_{2} \) produced from \( \text{BaO}_{2} \) is low in Ar because \( \text{O}_{2} \) evolves exclusively from the lattice when the peroxide is heated above \(600°C \) [Tribelhorn and Brown, 1995]. Additional high-temperature standards were generated by heating \( \text{O}_{2} \) gas to \(1000°C \) with platinum wire, which catalytically equilibrates oxygen isotopes in \( \text{O}_{2} \). These standards are used to correct for bulk composition-dependent nonlinearities on the IRMS.

Isotopic ordering was quantified by \(1\) comparing the measured \( \Delta_{36} \) and \( \Delta_{35} \) values against the \( \text{BaO}_{2} \) standard-derived ion correction and then \(2\) making a correction for the difference in bulk isotopic composition between standards and the unknown. These corrections are arithmetic corrections that were detailed in an earlier publication [Yeung et al., 2012]; long-term drifts in Ar content of the reference gas were corrected using the model described in Appendix A.

### 3.4. Experimental Results

Photochemical isotopic reordering occurred within several minutes inside the reaction bulb, with values of \( \Delta_{36} \) and \( \Delta_{35} \) reaching a steady state within \(5\) min at \(300\) \(K\). This rapid temporal evolution of \( \Delta_{36} \) and \( \Delta_{35} \) was reproduced by the photochemical model without altering any of the input parameters (see Figure 2).
calculated isotope exchange rates also yielded near-quantitative agreement between the experimental and the modeled steady state values at 300 K. Concentrations of other oxygen-containing species were kept low during these short experiments: Typical modeled concentrations at 300 K were \([O_2] \leq 2 \times 10^{13} \text{ cm}^{-3}, [O(\text{I})] \leq 10^5 \text{ cm}^{-3}\), and \([O(\text{P})] \leq 10^{11} \text{ cm}^{-3}\), compared with \(O_2\) number densities of \(10^{17} \text{ cm}^{-3}\).

The excellent agreement between the experiments and the model, for both \(\Delta_{36}\) and \(\Delta_{35}\), supports our hypothesis that \(O(\text{P}) + O_2\) isotope exchange reorders the isotopes in \(O_2\). Changes to the rates of the other reactions have no significant effect on the modeled values of isotopic ordering; only changes to the photon number density or the relative rates of isotope exchange altered the temporal evolution of \(\Delta_{36}\) and \(\Delta_{35}\). For example, excluding excited-state \(O_2(\Sigma)\) chemistry slows the model’s approach to steady state by ~15% and leaves the steady state \(\Delta_{36}\) and \(\Delta_{35}\) values nearly unchanged. To test the sensitivity of the model to irradiance, we simulated the temporal evolution of \(\Delta_{36}\) and \(\Delta_{35}\) for photon number densities ±30% about the a priori value of \(2.3 \times 10^{15} \text{ photons cm}^{-3} \text{s}^{-1} (254 \text{ nm})\) and \(2.6 \times 10^{15} \text{ photons cm}^{-3} \text{s}^{-1} (185 \text{ nm})\) calculated in section 3.2.1; the kinetics of the first several minutes of photolysis varied somewhat, but steady state values of isotopic ordering were reached within 5 min in all irradiance scenarios (see Figure 2).

Temperature variations are expected to have little effect on the overall kinetics of the laboratory experiments (although they affect the steady state \(\Delta_{36}\) and \(\Delta_{35}\) values). While \(O_2\) formation is faster at lower temperatures, the low pressures in the reaction vessel favor isotope exchange by at least a factor of \(10^5\) between 200 K and 400 K. Over this temperature range, we calculate that \(\Delta_{36}\) and \(\Delta_{35}\) reached steady state values within 10 min. The temperature of the quartz finger also reached a steady state after ~10 min. For the kinetics experiments described above, this initial warming of the quartz finger resulted in an uncertainty in the mean gas temperature, \(T_{gas}\), of ±2 K. For experiments maintaining a steady state for at least 10 min, the uncertainty in the mean gas temperature is also ±2 K, limited by the stability of the bath temperature.

Photolysis experiments, conducted for at least 40 min, had steady state \(\Delta_{36}\) and \(\Delta_{35}\) values that varied inversely with temperature. These steady state \(\Delta_{36}\) and \(\Delta_{35}\) values were similar to those predicted for isotopic equilibrium by ab initio calculations [see Table 3] [Wang et al., 2004]. However, while we observed good agreement between steady state and predicted equilibrium isotopic ordering at \(T > 300\) K, the steady state values for \(\Delta_{36}\) and \(\Delta_{35}\) at \(T < 300\) K were consistently lower than those predicted by theory (see Figure 3).

Despite this apparent disagreement between experiment and theory, we argue here that the experimental steady state values are true steady states that represent isotopic equilibrium. First, we conducted photolysis experiments in which the \(O_2\) sample was irradiated for 6 and 24 h in a ~78°C bath (218 K gas temperature) to determine if longer irradiation times resulted in an isotopic order closer to equilibrium. The resulting \(\Delta_{36}\) and \(\Delta_{35}\) values were indistinguishable from experiments lasting 40 min. Second, the steady state \(\Delta_{36}\) and \(\Delta_{35}\) values did not depend on the starting values: Experiments in which \(O_2\) was reordered from high \(\Delta_{36}\) and \(\Delta_{35}\) values to lower \(\Delta_{36}\) and \(\Delta_{35}\) values yielded steady state isotopic ordering that was indistinguishable from samples that were reordered starting at \(\Delta_{36} \Delta_{35} \sim 0\) (see Table 3). This behavior was reproduced in the photochemical model. Third, our analytical corrections yielded consistent \(\Delta_{36}\) values over a 5 month period; for example, experiments with \(O_2\) spanning 34% in \(\delta^{18}O\) yielded steady state \(\Delta_{36}\) values within ~0.1% during that time. The invariance of isotopic ordering, despite all these perturbations to the photochemical experiments and analyses, suggests that our 40 min photolysis experiments yielded a distribution of \(O_2\) isotopologues that closely resembles isotopic equilibrium.
If the photochemical reordering indeed yields equilibrium isotopic ordering, then only two mechanisms can explain the disagreement between experimental and theoretical $\Delta^{36}$ and $\Delta^{35}$ values: Either (1) the theoretical predictions overestimate isotopic ordering at equilibrium or (2) isotopic reordering is occurring during sample purification. While the theoretical predictions were based on the reduced harmonic partition function ratios, they are benchmarked by spectroscopic measurements, which suggest that anharmonic effects on the partition function would not be detectable at the current level of analytical precision ($\sigma \sim 0.1\‰$) [Robichaud et al., 2009]. We hypothesize, therefore, that isotopic reordering occurred during sample purification.

The absence of significant reordering during IRMS analysis and upon simple adsorption/desorption on the molecular sieve transfer fingers [Yeung et al., 2012] implicates the GC column as the site of isotopic reordering. To test this hypothesis, we compared the isotopic ordering of samples passed once through the GC column to those passed twice through the GC column. If reordering occurs on the GC column, samples passed twice through should exhibit departures from equilibrium values that are twice as large as those for single-pass samples.

Indeed, two-pass samples appeared more reordered than one-pass samples: $\Delta^{36}$ values of $O_2$ reordered at low temperatures were even lower after a second pass through the GC. In addition, high-temperature samples showed elevated $\Delta^{36}$ values, indicating that $O_2$ was being reordered toward a common measured value ($\Delta^{36} \sim 1.8\‰$) on the GC column. In contrast, isobaric interferences at $m/z = 36$ would only elevate $\Delta^{36}$ values (see Appendix A) instead of simultaneously depressing high $\Delta^{36}$ values and elevating low $\Delta^{36}$ values. These data suggest that the GC column catalyzed partial isotopic reordering, perhaps due to transition-metal impurities present on the molecular sieve 5A zeolite [Biermann and Janssen, 1989; Starokon et al., 2011]. Subsequent removal of the molecular sieve U-trap that was directly upstream of the GC system significantly improved isotopic ordering fidelity in several new GC columns that were installed after the data in this manuscript were acquired.

### Table 3. Photochemical Data for Steady State Experiments

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<th>$T_{\text{finger}}$/$^\circ\text{C}$</th>
<th>$T_{\text{gas}}$/K</th>
<th>$\Delta^{36}_{\text{measured}}$</th>
<th>$\Delta^{35}_{\text{measured}}$</th>
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<td>0.77</td>
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$^a$ $T_{\text{finger}}$ not measured directly; presumed to be equal to mean value for this $T_{\text{Bath}}$.

$^b$ Catalyzed by photolysis of $O_3$ in ambient light over a period of 2 months.

$^c$ Relative to atmospheric $O_2$. $^{18}O$ of $O_2$ used in photochemical experiments was $\sim –2\‰$. 

If the photochemical reordering indeed yields equilibrium isotopic ordering, then only two mechanisms can explain the disagreement between experimental and theoretical $\Delta^{36}$ and $\Delta^{35}$ values: Either (1) the theoretical predictions overestimate isotopic ordering at equilibrium or (2) isotopic reordering is occurring during sample purification. While the theoretical predictions were based on the reduced harmonic partition function ratios, they are benchmarked by spectroscopic measurements, which suggest that anharmonic effects on the partition function would not be detectable at the current level of analytical precision ($\sigma \sim 0.1\‰$) [Robichaud et al., 2009]. We hypothesize, therefore, that isotopic reordering occurred during sample purification.

The absence of significant reordering during IRMS analysis and upon simple adsorption/desorption on the molecular sieve transfer fingers [Yeung et al., 2012] implicates the GC column as the site of isotopic reordering. To test this hypothesis, we compared the isotopic ordering of samples passed once through the GC column to those passed twice through the GC column. If reordering occurs on the GC column, samples passed twice through should exhibit departures from equilibrium values that are twice as large as those for single-pass samples. Indeed, two-pass samples appeared more reordered than one-pass samples: $\Delta^{36}$ values of $O_2$ reordered at low temperatures were even lower after a second pass through the GC. In addition, high-temperature samples showed elevated $\Delta^{36}$ values, indicating that $O_2$ was being reordered toward a common measured value ($\Delta^{36} \sim 1.8\‰$) on the GC column. In contrast, isobaric interferences at $m/z = 36$ would only elevate $\Delta^{36}$ values (see Appendix A) instead of simultaneously depressing high $\Delta^{36}$ values and elevating low $\Delta^{36}$ values. These data suggest that the GC column catalyzed partial isotopic reordering, perhaps due to transition-metal impurities present on the molecular sieve 5A zeolite [Biermann and Janssen, 1989; Starokon et al., 2011]. Subsequent removal of the molecular sieve U-trap that was directly upstream of the GC system significantly improved isotopic ordering fidelity in several new GC columns that were installed after the data in this manuscript were acquired.
The preceding experimental results show that (1) only O(\(^3\)P) + O\(_2\) isotope exchange can explain the kinetics of \(\Delta_{35}\) and \(\Delta_{35}\) evolution and (2) the isotopic steady state is indistinguishable from isotopic equilibrium. The supporting data are consistent over a 5 month period, across several working-standard reference gases, GC columns, and IRMS tuning settings, indicating that analytical biases are unlikely. We conclude that O(\(^3\)P) + O\(_2\) isotope exchange drives the isotopic order of O\(_2\) to isotopic equilibrium.


Photochemical equilibration of O\(_2\) can be used to calibrate measurements of \(\Delta_{36}\) and \(\Delta_{35}\) in natural O\(_2\) samples (e.g., Figure 4). We used this calibration method to refine the \(\Delta_{36}\) and \(\Delta_{35}\) values in atmospheric O\(_2\) which our lab first reported in 2012. Over 14 months, samples of air (25 cm\(^3\)) were collected, between 7 and 10 A.M., in the UCLA Court of Sciences and prepared and analyzed according to the method described above. The high initial Ar content, however, required a second pass through the GC column to reduce residual \(^{36}\)Ar to the working range of \(~10\) ppb. We therefore used the relationship between \(\Delta_{35,\text{photolysis}}\) and \(\Delta_{35,\text{photolysis}}\) for two GC passes (see Figure 4) to correct measured values of \(\Delta_{35}\) for isotopic reordering on the GC column and the corresponding relationship to correct the measured values of \(\Delta_{35}\). The \(\pm2°C\) uncertainty in \(T_{\text{gas}}\) (primarily from \(T_{\text{bath}}\)) contributed \(\sim0.02\%\) uncertainty to \(\Delta_{36}\) and \(\sim0.01\%\) uncertainty in \(\Delta_{35}\).

Values of \(\Delta_{36}\) and \(\Delta_{35}\) showed no detectable drift during over 14 months. In addition, a Shapiro-Wilk normality analysis indicates that they are consistent with a normal distribution about their respective means, with \(\sigma_{\Delta_{35}} = 0.17\%\) and \(\sigma_{\Delta_{35}} = 0.3\%\) (\(p = 0.5\) and 0.3, respectively; see Figure 5). These standard deviations are similar to those observed for the calibration standards (e.g., \(\sigma_{\Delta_{36}} = 0.1\%\)), although the second pass through the GC likely decreased the reproducibility slightly. Mean values of isotopic order in UCLA air derived from this data collected. Furthermore, deliberate “poisoning” of one of those columns resulted in reordering that resembled the reordering reported here. We therefore hypothesize that some activating impurities had been transferred from the U-trap to the GC columns used in this study to cause partial O\(_2\) isotope reordering.

Plotting theoretical \(\Delta_{36}\) values against experimental values revealed the amount of reordering during each GC column pass. In such a plot, zero reordering would yield a slope of unity and an intercept of zero. Reordering toward \(\Delta_{36} \sim 1.8\%\) would result in a slope greater than unity and an intercept less than zero. For both single-GC and double-GC analyses, we observed a slope greater than unity and an intercept less than zero (Figure 4). Experimental and theoretical values are highly correlated in both cases. The magnitude of the slopes indicated isotopic reordering of \(~20\)% per pass on the GC column (\(d\Delta_{36,\text{theory}}/d\Delta_{36,\text{photolysis}} = 1.18 \pm 0.08; 2\sigma\)), and they are consistent with a doubling of isotopic reordering upon a second pass through the GC column (\(d\Delta_{36,\text{theory}}/d\Delta_{36,\text{photolysis}} = 1.49 \pm 0.06; 2\sigma\)). Reordering was neither observed unequivocally nor ruled out in \(\Delta_{35}\) values because of the smaller reordering signature expected (roughly half the magnitude observed in \(\Delta_{36}\) and the higher relative uncertainty in those measurements. From these data, we infer that the \(\Delta_{36}\) and \(\Delta_{35}\) values at steady state were near the theoretically predicted isotopic equilibrium values.

The preceding experimental results show that (1) only O(\(^3\)P) + O\(_2\) isotope exchange can explain the kinetics of \(\Delta_{36}\) and \(\Delta_{35}\) evolution and (2) the isotopic steady state is indistinguishable from isotopic equilibrium. The supporting data are consistent over a 5 month period, across several working-standard reference gases, GC columns, and IRMS tuning settings, indicating that analytical biases are unlikely. We conclude that O(\(^3\)P) + O\(_2\) isotope exchange drives the isotopic order of O\(_2\) to isotopic equilibrium.
set were $\Delta_{36} = 1.97 \pm 0.07\%$ and $\Delta_{35} = 1.0 \pm 0.1\%$ (2 s.e.; $n = 23$). These values of isotopic ordering in atmospheric $O_2$ are consistent with the values we reported previously, which had threefold to fourfold greater uncertainty.

The improved precision in the new data reported here reveal that the air sampled at UCLA is out of equilibrium with the annual mean local temperature (290 K), the annual mean global surface temperature (288 K), and also the annual mean midtropospheric temperature at ~5.5 km ($T_{trop} = 252$ K) [Vinnikov and Grody, 2003; Vinnikov et al., 2006], which could not be ruled out in our earlier study. The effective equilibrium temperature corresponding to our reported atmospheric $\Delta_{36}$ value is $260 \pm 5$ K, and the probability that it corresponds to $T_{trop}$ is $p < 0.01$.

5. Discussion

These data bolster the case that isotopic ordering in $O_2$ is altered by $O(3P) + O_2$ isotope exchange reaction throughout the atmosphere. High $O(3P)$ concentrations in the stratosphere, for example, will rapidly reorder the isotopes in $O_2$ there (see Figure 6) [Anderson, 1975; Anderson et al., 1985a; Brasseur and Solomon, 2005]. The kinetic rate coefficients for isotope exchange, which were verified in this study, further imply that the time scale of the reordering ranges from months to days, depending on altitude and attendant $O(3P)$ concentration. The low temperatures in the stratosphere should result in reordering to high $\Delta_{36}$ and $\Delta_{35}$ values ($\geq 2.5\%$ and $\geq 1.3\%$, respectively) before that air returns to the troposphere several years after entering the stratosphere [Holzer et al., 2012; Orbe et al., 2012]. Yet the measured tropospheric $\Delta_{36}$ and $\Delta_{35}$ values are significantly lower, implying reordering upon descent to ground level.

Isotopic ordering in the troposphere therefore represents a dynamic balance of physical and chemical influences: High $\Delta_{36}$ and $\Delta_{35}$ stratospheric air mixes continuously into the troposphere at a rate of $1-5 \times 10^{18}$ mol $O_2$ yr$^{-1}$ (the net $O_2$ flux depends on the precise definition of the tropopause) [Holton et al., 1995; Appenzeller et al., 1996; Yang and Tung, 1996; Schoeberl, 2004; Škerlak et al., 2014], so some form of chemical reordering is required to explain the lower $\Delta_{36}$ and $\Delta_{35}$ values observed in tropospheric air. This reordering mechanism must (1) drive isotopic ordering toward low $\Delta_{36}$ and $\Delta_{35}$ values and
(2) occur rapidly enough to balance the stratosphere-to-troposphere flux of $\Delta_{36}$ and $\Delta_{35}$. Biological cycling of O$_2$ is likely of limited importance, for example, because it is too slow by several orders of magnitude to counter the influence of stratospheric air mixing into the troposphere [Blunier et al., 2002].

Tropospheric O($^3P$) concentrations, in contrast, may be high enough to reorder O$_2$ to tropospheric values on the necessary time scales: The tropospheric trace gases NO$_2$ and O$_3$ both photolyze to produce O($^3P$), while the O($^3P$) + O$_2$ isotope exchange reaction proceeds quickly with no net consumption of that O($^3P$). Measured $\Delta_{36}$ and $\Delta_{35}$ values would then place constraints on where this isotope exchange chemistry must occur. Within ~5 km of the surface, typical daytime temperatures ($T_{trop} > 260$ K) are warm enough for photochemistry to drive isotopic ordering to the observed $\Delta_{36}$ and $\Delta_{35}$ values. At altitudes $\geq$ 5 km, however, photochemical isotope reordering would yield $\Delta_{36}$ and $\Delta_{35}$ values that are too high because the temperatures at those altitudes are too cold ($T_{trop} < 260$ K). Therefore, to explain the $\Delta_{36}$ and $\Delta_{35}$ values of tropospheric O$_2$, photochemical isotope reordering at low altitudes must presently outpace isotopic reordering at higher altitudes in the troposphere.

Intraannual and latitudinal variations in $\Delta_{36}$ and $\Delta_{35}$ may not be detectable at the current precision, especially if tropospheric isotope reordering in O$_2$ occurs on time scales much longer than the 1–2 year time scale tropospheric mixing [Waugh et al., 2013]. Using the annual rates of gas phase O$_2$ reordering and stratosphere-troposphere mass exchange, combined with first-order estimates of O($^3P$) concentrations in the troposphere ($\leq 5000$ cm$^{-3}$), the box model for $\Delta_{36}$ described by Yeung et al. [2012] indicates that isotopic ordering in atmospheric O$_2$ can vary on decadal time scales. However, the current null result does not rule out variations in isotopic ordering within the troposphere. Additional measurements of O$_2$ from different altitudes and latitudes as well as measurements of biological isotope fractionation will further constrain the balance of mechanisms yielding the present value of and potential atmospheric variations in O$_2$ isotopic ordering.

6. Conclusions

We have demonstrated that O($^3P$) + O$_2$ isotope exchange reactions rapidly reorder the isotopes in O$_2$ to equilibrium. We found that UV irradiation of pure O$_2$ yields steady state isotopic enrichments in $^{18}$O$^{18}$O.
and $^{17}$O$^{18}$O that agree with theoretical predictions over a range of temperatures. This photochemistry forms the core of a robust and precise method to calibrate measurements of isotopic ordering in $O_2$, i.e., $\Delta_{36}$ and $\Delta_{35}$. While some isotopic reordering can occur during sample purification, the extent of reordering can be routinely quantified and corrected, as demonstrated by the long-term stability of the calibration and of tropospheric air measurements at UCLA.

The photochemical scheme described here provides an invaluable and rigorous link between theoretical predictions and laboratory measurements of isotopic ordering in $O_2$. Moreover, it can be replicated easily in different laboratory settings and interfaced with different measurement techniques. Thus, the photochemistry scheme described here constitutes a practical standardization technique for future studies of $O_2$ in the fields of biogeochemistry, atmospheric chemistry, and quantitative spectroscopy. At present, the method’s accuracy is primarily limited by uncertainties arising from sample processing and analysis, and to a lesser extent, the accuracy of the modeled in situ reaction temperature. Future refinements of the photochemical scheme will concentrate on minimizing internal temperature gradients and removing residual ozone for long-term storage. Improvements in mass spectrometric resolution should reduce long-term analytical uncertainties by reducing the amount of sample handling required.

The kinetics of the $O(3P) + O_2$ isotope exchange reaction have significant implications for the interpretation of $\Delta_{36}$ and $\Delta_{35}$ values in nature. Ground-state atomic oxygen is ubiquitous in the atmosphere, so isotopic reordering via $O(3P) + O_2$ likely controls isotopic ordering in $O_2$ wherever gas phase photochemistry is important. In restricted and aqueous environments, where $O(3P)$ is not generated, other bond-altering processes will dominate. For example, photosynthetic water splitting and respiratory $O_2$ consumption, which are irreversible redox processes, should yield unique and likely nonequilibrium signatures on the generated and residual $O_2$, respectively. Isotopic ordering offers a window into the chemical physics of these processes as well as their contributions to the mass balance of $O_2$ in natural environments.

**Appendix A: Ion Corrections**

Empirical ion corrections are used in a variety of isotopologue analysis [Huntington et al., 2009; He et al., 2012; Yeung et al., 2012; Stolper et al., 2014], but they have scarcely been investigated in depth. The ion corrections in $O_2$ isotopologue analysis are especially challenging, so we present a model here that serves as a template for generating similar corrections in other systems.

Our previous work identified two main sources of unwanted ion current at the mass spectrometer’s $m/z = 36$ Faraday cup: $^{36}Ar^+$ and a peak tail from other $O_2^+$ isotopologues. Measurements of $^{40}Ar$ were used as a proxy for $^{36}Ar$ content, specifically the voltage ratio between $^{40}Ar$ in the sample and in the laboratory working standard, i.e., $V_{40,SA}/V_{40,ST}$. This ratio can be measured precisely, but it is susceptible to long-term drift when the Ar content of the laboratory working standard changes. Chemical fractionation and atmospheric leaks, which occurred during the expansion of daily standard aliquots into the IRMS bellows, yielded noticeable drift in the ion correction over time scales of weeks or longer. An expression for the dependence of $\Delta_{36}$ on $V_{40,ST}$ was therefore derived to model this behavior. By defining the measured $m/z = 36$ voltage as the sum of $^{18}O^{18}O^+$ and $^{36}Ar^+$ contributions, i.e., $V_{36} = V_{36O_2} + V_{36Ar}$, the resulting 36/32 isotopologue ratio, $\frac{36}{32}_{\text{measured}}$, becomes

$$\frac{36}{32}_{\text{measured}} = \frac{\left(\frac{V_{36O_2,SA} + V_{36Ar,SA}}{V_{32,SA}} \right)}{\left(\frac{V_{36O_2,ST} + V_{36Ar,ST}}{V_{32,ST}} \right)} \quad (A1)$$

where the subscript numbers refer to cardinal masses of each species and SA and ST refer to sample and standard, respectively. The stochastic 36/32 isotopologue ratio, $\frac{36}{32}_{\text{stochastic}}$, is calculated from the 34/32 isotopologue ratio, which is accurate to ~2 ppm when all $m/z = 34$ signal is assumed to be $^{16}O^{18}O$:

$$\frac{36}{32}_{\text{stochastic}} = \left(\frac{\frac{V_{34,SA}}{V_{32,SA}}}{\frac{V_{34,ST}}{V_{32,ST}}} \right)^2 \quad (A2)$$
Finally, we substitute $V_{36\text{Ar}} = kV_{40}$, where $k$ is a proportionality factor accounting for both the relative $^{36}\text{Ar}/^{40}\text{Ar}$ abundance and instrumental mass fractionation effects. After imposing the laboratory pressure-balancing condition, i.e., $V_{32,\text{SA}} = V_{32,\text{ST}}$, the equation reduces to

$$
\Delta_{36,\text{measured}} = \left[ \frac{kV_{40,\text{ST}}}{V_{36\text{O}_2,\text{ST}} + kV_{40,\text{ST}}} \left( \frac{V_{34,\text{ST}}}{V_{34,\text{SA}}} \right)^2 \left( \frac{V_{40,\text{SA}}}{V_{40,\text{ST}}} \right) + \left( \frac{V_{36\text{O}_2,\text{SA}}}{V_{36\text{O}_2,\text{ST}} + kV_{40,\text{ST}}} \left( \frac{V_{34,\text{ST}}}{V_{34,\text{SA}}} \right)^2 - 1 \right) \right].
$$

(A3)

Equation (A3) defines a line relating two measured quantities, $\Delta_{36,\text{measured}}$ and $V_{40,\text{SA}}/V_{40,\text{ST}}$, with a slope and intercept that depend on (1) the $^{36}\text{Ar}$ content of the working-standard gas and the (2) bulk $\delta^{18}\text{O}$ composition. As $V_{40,\text{SA}}/V_{40,\text{ST}}$ increases, the magnitude of both the slope and intercept increases. They also vary inversely with $V_{34,\text{SA}}/V_{34,\text{ST}}$, the bulk isotopic composition. These variations are approximately linear over the range of $V_{40,\text{ST}}$ we have measured.

Consideration of the $^{36}\text{Ar}$ isobar alone, however, is insufficient to account for the laboratory data; a peak tail and/or another isobar (e.g., H$^{25}\text{Cl}$) may be important. By casting $V_3 = V_{36\text{O}_2} + V_{36\text{Ar}} + V_{\text{tail}}$, equation (A3) becomes

$$
\Delta_{36,\text{measured}} = \left[ \frac{kV_{40,\text{ST}}}{V_{36\text{O}_2,\text{ST}} + kV_{40,\text{ST}} + V_{\text{tail,ST}}} \left( \frac{V_{34,\text{ST}}}{V_{34,\text{SA}}} \right)^2 \left( \frac{V_{40,\text{SA}}}{V_{40,\text{ST}}} \right) + \left( \frac{V_{36\text{O}_2,\text{SA}}}{V_{36\text{O}_2,\text{ST}} + kV_{40,\text{ST}} + V_{\text{tail,ST}}} \left( \frac{V_{34,\text{ST}}}{V_{34,\text{SA}}} \right)^2 - 1 \right) \right].
$$

(A4)

The form of equation (A4) is similar to that of equation (A3), but with one notable difference: The intercept of the $\Delta_{36,\text{measured}}$ versus $V_{40,\text{SA}}/V_{40,\text{ST}}$ plot varies directly with $V_{\text{tail,SA}}$. Note that the dependence of the $\Delta_{36,\text{measured}}$ versus $V_{40,\text{SA}}/V_{40,\text{ST}}$ plot on bulk isotopic composition is weak; a peak tail from other $^{18}\text{O}$ isotopologues that depends on the bulk isotopic composition (i.e., $V_{\text{tail,SA}}$ increases with $V_{34,\text{SA}}$) would amplify that dependence. Indeed, we observed a dependence of the $\Delta_{36,\text{measured}}$ versus $V_{40,\text{SA}}/V_{40,\text{ST}}$ intercept on bulk isotopic composition, suggesting that this additional correction is justified [Yeung et al., 2012].

To account for drift in $V_{36\text{Ar,ST}}$ and $V_{\text{tail,SA}}$ simultaneously, two types of standard gases were measured consistently during analytical sessions. First, high-temperature standards generated from BaO$_2$ decomposition were measured over a range of $V_{40,\text{SA}}/V_{40,\text{ST}}$ values. Probing a large range in $V_{40,\text{SA}}/V_{40,\text{ST}}$ over time allows one to monitor the changing slope and intercept of a $\Delta_{36,\text{measured}}$ versus $V_{40,\text{SA}}/V_{40,\text{ST}}$ plot. Second, high-temperature standards generated by heating working-standard O$_2$ to 1000°C were measured. These secondary standards had $\delta^{18}\text{O}$ values different from those generated by BaO$_2$ decomposition; measuring $\Delta_{36}$ at two different $\delta^{18}\text{O}$ values allows one to account for bulk composition-dependent nonlinearities.

We allowed the slope and intercept of equation (A4) to evolve linearly with time, constrained by the BaO$_2$-derived standards. To arrive at a best fit time evolution of the slope and intercept, we varied the slope and intercept values at the beginning and end of each analytical period (four variables) such that the sum of squared deviations from the BaO$_2$-derived standards was minimized over the entire period. The resulting linear trends yielded a slope and intercept for each day of an analytical run; these parameters were used for the ion correction for all analyses conducted on that day. One check for the consistency of this method over time was the secondary standards (working-standard O$_2$ heated to 1000°C). Values of $\Delta_{36}$ of the secondary standards showed consistent deviations from the primary BaO$_2$-derived $\Delta_{36,\text{measured}}$ versus $V_{40,\text{SA}}/V_{40,\text{ST}}$ lines, confirming the presence of bulk composition-dependent nonlinearities. Gases with lower $\delta^{18}\text{O}$ had higher $\Delta_{36,\text{measured}}$ values, whereas gases with higher $\delta^{18}\text{O}$ had lower $\Delta_{36,\text{measured}}$ values, compared to the BaO$_2$-derived standards. These departures were constant over the course of analytical periods, when the IRMS source tuning parameters and ion optics remained unchanged. Both sets of standards displayed similar external standard deviations about the mean of 0.1–0.2‰.

References


