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Isotopic fractionation of nitrous oxide in the stratosphere: Comparison between model and observations

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[1] We investigate the mass dependent isotopic fractionation mechanisms, based on photolytic destruction and reaction with O(1D), to explain the 15N/14N and 18O/16O fractionation of stratospheric N2O and reconcile laboratory experiments with atmospheric observations. The Caltech/JPL two-dimensional (2-D) model is utilized for detailed studies of N2O and its isotopologues and isotopomers in the stratosphere. We compare model results with observations of isotopic enrichment using three different methods of calculating photolytic cross-sections for each of the major isotopologues and isotopomers of N2O. Although the Yung and Miller [1997] successfully modeled the pattern of enrichments for each isotopologue or isotopomer relative to each other, their approach underestimated the magnitude of the enrichments. The ab initio approach by Johnson et al. [2001] provides a better fit to the magnitudes of the enrichments, with the notable exception of the enrichment for the 15N14N16O. A simpler, semi-empirical approach by Blake et al. [2003] is able to model the magnitude of all the enrichments, including the one for 15N14N16O. The Blake et al. [2003] cross-sections are temperature-dependent, but adjustments are needed to match the measurements of Kaiser et al. [2002a]. Using these modified cross-sections generally improves the agreement between model and mass spectrometric measurements. Destruction of N2O by reaction with O(1D) results in a small but nonnegligible isotopic fractionation in the lower stratosphere. On a per molecule basis, the rates of destruction of the minor isotopologues or isotopomers are somewhat less than that for 14N14N16O. From our 2-D model we infer the relative rates for isotopologues and isotopomers 14N18N18O (446), 14N15N16O (456), 15N14N16O (546), 14N14N17O (447) and 14N15N18O (448), to be 1.0, 09843, 09942, 09949, and 09900, respectively. Thus the destruction of N2O in the atmosphere results in isotopic fractionations of (456), (546), (447) and (448) by 19.4, 9.5, 5.5 and 12.0%o. If we do not distinguish between the (456) and (546) isotopomers, the mean isotopic fractionation for 15N is 14.5%. If we assume that the mean tropospheric values for δ456, δ546, δ15N and δ18O are 16.35, -2.35, 7.0 and 20.7%, respectively, we infer the following isotopic signature for the integrated sources of N2O: δ456 = -2.9%o, δ546 = -11.7%o, δ15N = -7.3%o and δ18O = 8.7%o.

INDEX TERMS: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0341 Atmospheric Composition and Structure: Middle atmosphere—constituent transport and chemistry (3334); 1040 Geochemistry: Isotopic composition/chemistry; 1610 Global Change: Atmosphere (0315, 0325); 1615 Global Change: Biogeochemical processes (4805); KEYSWORDS: isotope, N2O, stratosphere


1. Introduction

[2] The present terrestrial atmosphere contains about 310 ppbv (1 part per billion by volume = 1 nmol mol-1 [Prinn et al., 2000]) of nitrous oxide (N2O). N2O is produced mainly by microbes as a part of the nitrogen cycle [Stein and Yung, 2003]. It is removed from the atmosphere primarily by photodissociation

\[ \text{N}_2\text{O} + \text{h} \rightarrow \text{N}_2 + \text{O}(^1\text{D}) \]

(1)

with a smaller loss (~10%) from the photo-oxidation reaction with O(1D)

\[ \text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow 2 \text{NO} \]

(2a)

\[ \rightarrow \text{N}_2 + \text{O}_2 \]

(2b)
It is convenient to summarize the rate of destruction of N$_2$O as a linear process $L_X$, where $X$ is the mixing ratio of N$_2$O, and $L$ is the loss coefficient due to the above processes

$$L = J_1 + (k_{2a} + k_{2b})[O(1D)]$$  

(3)

where $J_1$ is the photodissociation rate constant for reaction (1) and $k_{2a}$ and $k_{2b}$ are the rate constants for reactions (2a) and (2b). Both reactions (1) and (2) take place primarily in the stratosphere, resulting in a mean lifetime of about 120 years for N$_2$O [Minschwaner et al., 1993; Olsen et al., 2001]. Reaction (2a) is the major source of odd nitrogen (NO$_x$) to the stratosphere and plays a fundamental role in regulating the ozone layer [see, e.g., Logan et al., 1978; Wennberg et al., 1994].

[1] On a per molecule basis, N$_2$O is about 206 times as effective as CO$_2$ in causing global warming in the present atmosphere [Houghton et al., 1990]. A doubling of atmospheric N$_2$O would cause the mean global surface temperature to increase by 0.7°C [Wang et al., 1976; Houghton et al., 1990, 2001], which is approximately the total observed mean global warming in the last hundred years. An increase in atmospheric N$_2$O was predicted to occur in connection with enhanced agricultural activity [McElroy et al., 1977]. However, there was disagreement on the projected rate of increase of N$_2$O [see, e.g., Yung et al., 1976]. The actual rate of increase has been determined by high precision gas chromatography measurements of atmospheric flask samples. The data suggest that the rate of N$_2$O increase was about 0.5–0.6 ppbv yr$^{-1}$ during 1976–82, increased to 0.8–1 ppbv yr$^{-1}$ in 1988–90, and returned to a rate of 0.5–0.6 ppbv yr$^{-1}$ in recent years [Weiss, 1981; Zander et al., 1994; Khalil and Rasmussen, 1995]. In addition, it has been found that during the last ice age (18,000 years ago), the atmosphere contained only 200 ppbv of N$_2$O [Leuenberger and Siegenthaler, 1992; Flückiger et al., 1999], as compared to the preindustrial value of 280 ppbv. The present N$_2$O concentration in the atmosphere is 55 and 11% above the ice age and preindustrial values, respectively. While the increase of N$_2$O from the ice age to the preindustrial level was clearly part of the natural climate/biosphere cycle, the increase from the preindustrial to the present level was most likely caused by human activities. The historical increase of N$_2$O is likely to continue into the future.

[4] The continued increase of N$_2$O in the atmosphere is a serious environmental concern for the reasons stated above. As a consequence, N$_2$O is one of the gases targeted for regulation by the Kyoto Protocol (available at http://www.isid.ca/climate/kyoto), the other gases being CO$_2$, CH$_4$, SF$_6$, hydrofluorocarbons and perfluorocarbons. According to a recent analysis [Nevison and Holland, 1997], the current increase rate, 0.6–1 ppbv yr$^{-1}$, or 0.2–0.3% per year, represents an excess of 30–50% of global emissions over current sinks. Therefore to stabilize concentrations at the present level, an immediate reduction of 70–80% of the additional flux of N$_2$O that has occurred since the industrial revolution would be necessary. Without immediate steps taken to regulate N$_2$O emissions, the atmospheric concentration is expected to rise to 400–500 ppbv, or about twice the preindustrial concentration. However, the N$_2$O budget is at present not well quantified, making it difficult to determine the sources and the cause of its increase precisely [Houghton et al., 1996; Cicerone, 1989; Khalil and Rasmussen, 1992]. Houghton et al. [2001, Table 4.4] summarizes the current knowledge of the budget of N$_2$O. The range of uncertainty is quite large, exceeding a factor of two in many cases. This is obviously an unsatisfactory state of knowledge for a gas that we wish to regulate. We shall argue that an understanding of the isotopes of N$_2$O is the key to a better budget of the sources of N$_2$O.

[5] A most powerful method for characterizing the sources of N$_2$O lies in its multi-isotope signature, as demonstrated in the seminal work by Kim and Craig [1993] (hereafter referred to as KC93). (Kaiser et al. [2002a] pointed out the largely ignored preKC93 work on isotopic fractionation.) The significant results of KC93 are: (1) the major land biospheric sources of N$_2$O are light in both $^{15}$N and $^{18}$O, relative to tropospheric N$_2$O, (2) stratospheric N$_2$O is heavy in both $^{15}$N and $^{18}$O, relative to tropospheric N$_2$O, and (3) there must be a large “back flux” of heavy N$_2$O from the stratosphere to the troposphere in order to account for the isotopic composition of tropospheric N$_2$O. Therefore if we could compute (4) in an atmospheric model, we would have a constraint on the isotopic composition of the biological source.

[6] This paper is focused on the isotopic fractionation of N$_2$O in the stratosphere and its implications for the budget of N$_2$O. Following a discussion of the mechanisms and observations, we use the Caltech/JPL two-dimensional (2-D) model to simulate the observed isotopic fractionations of N$_2$O in the stratosphere. A tentative budget for the isotopic source from the biosphere is deduced from this study. This work complements a recent study of the same subject with emphasis on the $^{15}$O anomaly using a 3-D model [McLinden et al., 2003].

2. Isotopic Fractionation of N$_2$O: Mechanisms and Observations

[7] There are three important isotopologues of N$_2$O: $^{15}$NNO, N$_2^{16}$O and N$_2^{17}$O. In addition, there are two $^{15}$N isotopomers of N$_2$O: $^{15}$N$^{14}$NO and N$_2^{15}$O. For definitions of “isotopologue” and “isotopomer”, the reader is referred to the International Union of Pure and Applied Chemistry (IUPAC) Compendium of Chemical Terminology 2nd Edition [1997]. Hereafter, we will refer to $^{15}$N$^{14}$N$^{15}$O, $^{15}$N$^{14}$N$^{16}$O, $^{15}$N$^{14}$N$^{17}$O, $^{15}$N$^{14}$N$^{18}$O and $^{15}$N$^{14}$N$^{19}$O as (446), (456), (546), (447) and (448), respectively. N$^{15}$NO (N$^{17}$NO and N$^{19}$NO) and N$^{15}$NO ($^{17}$NO) are also used in the literature to denote the central and terminal positions of the N atom in N$_2$O, respectively. See Kaiser et al. [2002a, Appendix] for a detailed discussion.

[8] For the isotopic fractionation of isotopologues and isotopomers of N$_2$O, it is convenient to adopt the $\delta$ notation, defined as follows:

$$\delta_i(\%o) = \left( \frac{R_i}{R_{std}} - 1 \right) \times 1000$$  

(4)

where $R_i = ( ^{15}$N$^{14}$N$) / ( ^{17}$O$^{16}$O$)$ or ( $^{18}$O$^{16}$O$)$ in the sample of interest, and $R_{std}$ is same ratio in a standard sample [O’Neil, 1986]. For the purposes of this study, the values of $R_{std}$ based on elemental abundances, are 0.003690, 0.003690, 0.0003729 and 0.002039 for (456), (546), (447) and (448), respectively. As the destruction of N$_2$O is characterized by a
linear loss mechanism, the fractionation of isotopically substituted N₂O can be considered a Rayleigh fractionation process, which is described by the following ratio:

$$\frac{(\delta_i + 1)}{(\delta_0 + 1)} = f_{\epsilon}^{\text{c}}$$  \hspace{1cm} (5)

In Equation (5), \(\delta_i\) is the delta value for isotopologue or isotopomer \(i\), while \(\delta_0\) is the delta value in the troposphere. The quantity \(f\) is the fraction of N₂O remaining in the parcel of air and \(\epsilon_i\) is the measured rate of fractionation, also known as the enrichment, for isotopologue or isotopomer \(i\) in the stratosphere. Taking logarithms of both sides, we have

$$\ln[(1 + \delta_i)/(1 + \delta_0)] = \epsilon_i \ln f$$  \hspace{1cm} (6)

If we make the approximation that \(\ln(1 + \delta) \approx \delta\) for \(\delta \ll 1\), a linear relationship between \(f\) and \(\delta_i\) can be derived, \(\delta_i \approx \delta_0 \epsilon_i + \epsilon_i \ln f\), where \(\epsilon_i\) is the slope of the line. However, this is a poor approximation for N₂O studies [see Kaiser et al., 2002a, Appendix]. For example, for \(\delta_i = 100\%\), \(\ln(1 + \delta_i) = 95.3\%\) and the difference between the two is 4.7\%, an unacceptably large error. Unless otherwise stated, we will use (6) in this paper. The enrichment \(\epsilon_i\) [see, e.g., Toyoda et al., 2001] is not the same as the fractionation constant [see, e.g., Kaiser et al., 2002a; McLinden et al., 2003], except in a limiting case. For a detailed relation in a 1-D model, see equations (B27–B28) in Appendix B. There should be no confusion because the context in which they are used is different.

[9] Following the discovery of the N₂O isotopic anomaly by KC93; Johnston et al. [1995] attempted to verify the suggestion that stratospheric chemistry results in N₂O isotopic fractionation. However, laboratory experiments measured very little isotopic enrichment in photolyzed or photo-oxidized N₂, 16O/N₂, 15O/N₂, 18O samples. These studies and the possibility of an unidentified reaction in the stratosphere have led to several proposals for new sources of N₂O in the upper atmosphere [McElroy and Jones, 1996; Prasad, 1994, 1997, 1998; Zipf and Prasad, 1998]. Yung and Miller [1997] (hereafter referred to as YM97) pointed out that the photodissociation experiments of Johnston et al. [1995] did not provide a definitive test of photolysis as a mechanism for fractionation because these experiments were performed at 185 nm [see also Kaiser et al., 2003], sampling a portion of the absorption spectrum near the cross-section maximum. Here the value of the cross-section is particularly insensitive to a spectral shift caused by isotopic substitution of the N₂O molecule. The bulk of atmospheric N₂O photodestruction occurs around 200–202 nm due to the convolution of the N₂O absorption cross-sections with the atmospheric UV transmission window [Minschwerner et al., 1993]. Mindful of this, YM97 proposed a wavelength-dependent mechanism for the photolytic fractionation of N₂O based on subtle shifts in the zero point energies (ZPE) with isotopic substitution. For example, substituting 18O for 16O results in a calculated ZPE blue shift for the heavier isotopologue of −27.5 cm⁻¹. While the cross-sections are essentially identical at the absorption peak, a clear separation is manifest on both shoulders. Analogous to the kinetic fractionation for a chemical reaction, the photolysis fractionation factor will be equal to the ratio of the heavy-to-light photolysis rates and thus to the ratio of the cross-sections. For N₂O, the theoretical fractionation can be calculated analytically as a function of wavelength using the spectral function of Selwyn et al. [1977], and the YM97 model was able to match, at least qualitatively, the observed enrichments of both 15N and 18O.

[10] Photolysis experiments investigating the validity of the YM97 theory were performed by Rahn et al. [1998], Röckmann et al. [2000], Turatti et al. [2000], and Zhang et al. [2000]. The data are clearly consistent with a simple Rayleigh fractionation model, and the trend of the heavy isotope enrichment with wavelength were consistent with that predicted by YM97. It was observed that enrichments of 15N to 18O yields ratios that were slightly greater than unity at wavelengths close to the effective or mean stratospheric photolysis wavelength of 205 nm. This is nearly identical to the ratio of the enrichments observed in Rahn and Wahlen [1997] and close to that predicted in Figure 2 of YM97; it supports the hypothesis that photolysis is the principal mechanism responsible for the observed stratospheric enrichments and that the standard model of stratospheric N₂O chemistry is essentially complete. Turatti et al. [2000] and Zhang et al. [2000] observed that the enrichment for the 14N, 15N, 16O was greater than that for the isotopomer 15N, 15N, 16O, as predicted by YM97. The magnitudes of the experimentally determined enrichments were all found to be much greater than that predicted by YM97, however. For example, the 18O enrichment at 207.6 nm was found to be −46.0 ‰, more than twice that predicted by YM97.

[11] Several papers have reported observations of N₂O isotopic fractionation in the stratosphere. Information about these measurements is presented in Table 1. Griffith et al. [2000] (Griffith et al., manuscript with revisions, 2003; Griffith, private communication, 2003) analyzed Fourier Transform Spectrometer (FTS) data collected through limb sounding on a balloon platform, while Rahn and Wahlen [1997], Röckmann et al. [2001] and Toyoda et al. [2001] report on direct stratospheric sampling followed by analysis using a mass spectrometer. The two latter mass spectrometer studies were able to differentiate between the 14N, 15N, 16O and 15N, 14N, 16O isotopomers by examining the 14N, 16O and 13N, 16O fragments. The results of these observations are consistent with the laboratory results; while the pattern of isotopic enrichment between isotopologues and isotopomers is predicted by YM97, the magnitude of these effects is

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<th>Table 1. Isotopic Fractionation of N₂O—Stratospheric Observations</th>
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¹MS, Mass Spectrometer; FTS, Fourier Transform Spectrometer.
greater in the observations than what is predicted by theory. For example, the $^{18}$O stratospheric enrichment of Toyoda et al. [2001] was found to be $-24.6\%_{\text{C}0}$. YM97 predicts an enrichment of $-13.2\%_{\text{C}0}$. The enrichment values deduced from the FTS measurements were about 55–80% higher than those of the mass spectrometric (MS) measurements, and the errors associated with the FTS enrichment were between 17 and 70%.

[12] Theoretical modeling to extend photodestruction induced isotopic fractionation to include other aspects of photolysis was carried out by Johnson et al. [2001] and Blake et al. [2003]. A full description of the approach used by Johnson et al. [2001] can be found in their paper. The factors included in their theoretical description of heavy isotopologue or isotopomer enrichment by photolysis are (1) ZPE shift, (2) excited-state potential energy surfaces, (3) bending mode excitation in the ground electronic state, (4) the transition dipole surface, and (5) the initial wave function. The net effect of these factors is that the magnitude of the isotopologue and isotopomer enrichment is greater than that calculated by YM97. Since the emphasis of Johnson et al. [2001] was on deriving the photolytically-driven enrichment and not on reproducing the N$_2$O ultraviolet absorption curve, there is about a 3 nm difference between the theoretical absorption profile reported and the standard absorption curve that NASA recommends [DeMore et al., 1997]. In order not to avoid spurious effects due to differences between the theoretical and standard absorption curves, the theoretical absorption profiles were renormalized with respect to the standard profiles of DeMore et al. [1997].

[13] The approach of Blake et al. [2003] is to describe the changes to the absorption profile with a pseudo-diatomic molecule Born-Oppenheimer model. Further details of the theory will be presented in a paper by M. C. Liang et al. (A semi-analytic model for photo-induced isotopic fractionation in simple molecules, manuscript submitted to Journal of Geophysical Research, 2003), but we review the salient details here. This method takes advantage of the fact that we are not interested in the absolute value of the absorption profile for each isotopologue or isotopomer but rather in the small changes between the main isotopologue and the others. In the Born-Oppenheimer limit, the electronic ground state and excited potential energy surfaces are independent of isotopic substitution. However, the vibrational wave functions are affected with changes in geometry leading to shifts in the absorption cross-sections (similar to that envisioned in YM97) and changes in eigenstate energy (the ZPE shifts) leading to changes in the shape of the absorption cross-sections. If the vibrations are treated as slightly anharmonic oscillators, the absorption cross-sections may be fit as the product of an isotopically-independent polynomial of order five with an isotopologue-specific Gaussian function. The polynomial function accounts for the curvature of the electronically excited potential energy surface and the variation of the dipole matrix element with geometry, and the results of such a fit to the $^{15}$N$^{14}$N$^{18}$O are shown in Figure 1a. The sharp structure in the cross-section above energies of 50,000 cm$^{-1}$ arises from absorption out of excited bending states of nitrous oxide. Provided the vibrational frequencies of all the isotopologues and isotopomers are known, their cross-sections can be accurately calculated using only experimental data. In all systems investigated to date (the hydrogen halides, water, ozone, and nitrous oxide), the ZPE-induced shape changes dominate over the cross-section shifts, resulting in a fractionation pattern that is strongly curved with frequency.

[14] For N$_2$O, the excited electronic state has a nonlinear minimum, which leads to poor Franck-Condon overlap with the vibrational ground state. The total absorption profile is therefore fit as a temperature dependent sum of three Gaussians corresponding to the absorption profile of the ground vibrational state and the first two excited bending states. The parameters associated with each profile were found using measurements over a range of temperatures. The standard N$_2$O absorption profiles were done using data measured with wavelengths less than 200 nm. Including the measurements of Yoshino et al. [1984] and Méridenne et al. [1990] insures that data associated with the wavelength region of photolysis critical to the stratosphere (~201 nm) is used in the parameterization.

[15] A comparison between the three cross-section models and laboratory data is shown in Figure 1b. The laboratory measurements are taken from Rahn et al. [1998], Röckmann et al. [2000, 2001], Turatti et al. [2000], Zhang et al. [2000], data reanalyzed by D. Griffith, Griffith, private communication, 2003, and Kaiser et al. [2002b]. The data are represented in Figure 1b as a plot of $(\sigma/\sigma_{346} - 1)$ versus photolysis wavelength, where $\sigma$ and $\sigma_{346}$ are photodissociation cross-sections for isotopologue or isotopomer (i) and (446), respectively. In general, the semi-empirical model of Blake et al. [2003] predicts more fractionation than the other two models. As discussed in their paper, the ZPE model of YM97, which is the straight dotted line on the graphs, lacks the curvature needed to match the data, since it only considers one of the factors leading to isotopic fractionation by photolysis. If the fractionation curves for each of the isotopologues are examined in detail, it can be seen that the pseudo-diatomic model of Blake et al. [2003] provides a better match for the laboratory data of the $^{15}$N substituted isotopologues and isotopomers of N$_2$O than the other two models. In particular, the semi-empirical model does not have the 205 nm “hump” in the (546) isotopomer enrichment curve predicted by the ab initio model (dashed line in Figure 1b) of Johnson et al. [2001]. The most likely cause of the discrepancy is the assumption that the N-N bond length is fixed [McLinden et al., 2003]. The Born-Oppenheimer model also provides as good a match to the $^{18}$O substituted isotopologue of N$_2$O as the ab initio model.

[16] Recently, Kaiser et al. [2002a] measured the fractionation factors for N$_2$O from 193 to 295 K at 207 nm. The temperature-dependent cross-sections for (448), (456), and (546) have been computed by Blake et al. [2003] at all wavelengths and temperatures relevant to the stratosphere. A detailed comparison between Kaiser et al. [2002a] and Blake et al. [2003] will be given in Liang et al., [2003, manuscript in preparation, 2003], (456) is in good agreement with the measurements, with difference <5%. However, the model values for (448) and (546) differ significantly from that of the laboratory measurements, about 5% at room temperature and reaching 10–15% at 210 K. In order to test the impact of Kaiser et al.’s [2002a] measurements in our model, we modified the cross-sections of Blake et al. [2003] to match the 207 nm measurements. The temperature-dependent adjustment factors are then
uniformly applied to the whole wavelength region. We do not have temperature-dependent measurements of the cross-sections for (447). The adjustment is scaled from (448). The net result is that the modified Blake et al. [2003] cross-sections are within 1\% of the original cross-sections. Kaiser et al. [2002b] reported measurements of N2O fractionation in its reaction with O(1D) atoms. Their room temperature data show enrichment of 8.79\% for (546), 2.22\% for (456) and 12.23\% for (448). Although this channel for N2O loss is very small over the entire stratosphere, in the lower parts of the stratosphere its contribution can be significant. The authors suggest that fractionation from this channel might explain the fact that the observed ratio of enrichment of 14N15N16O over enrichment of 15N14N16O is smaller than would be expected if only photolysis and transport influenced fractionation.

3. Two-Dimensional Chemical Transport Model

We use the Caltech/JPL 2-D model for simulating the distribution of N2O in the atmosphere. The continuity equation

\[ \frac{\partial \chi}{\partial t} + \nabla \cdot \left( \mathbf{v} \chi \right) + w \frac{\partial \chi}{\partial z} - \frac{1}{\cos \theta} \frac{\partial}{\partial \theta} \left( \cos \theta K_{yy} \frac{\partial \chi}{\partial \theta} \right) - \frac{\epsilon K_{zz}}{\epsilon K_{zz} + K_{zz}} \frac{\partial \chi}{\partial z} = \frac{Q}{M} \]  

(7)

is solved for all important, long-lived species where \( \chi \) is the mixing ratio for the species. The details of the model are in appendix A. The model uses NASA recommendations for stratospheric modeling of the rate constants of the gas phase reactions [DeMore et al., 1997]. The chemical destruction reactions of N2O, listed in Equations (1) and (2), are discussed in the Introduction. For completeness, the production channel of N2O

\[ \text{N}_2 + \text{O}(1D) + \text{M} \rightarrow \text{N}_2\text{O} + \text{M} \]  

(8)

is also included. The model is run for 13 years, during which climatological and radiation updates to the model are done monthly. A standard mixing ratio of 3.1 \times 10^{-7} for N2O is used to start the run. For the minor isotopologues and isotopomers, the initial concentrations and the rates of N2O production are calculated using the standard isotopic ratios. For all the runs, only the concentrations of N2O and O(1D) are allowed to vary. Concentrations of ozone are fixed using the climatology recommended by the SPARC [Fortuin and Kelder, 1998; Randel and Wu, 1999]. The model is run with each set of photolytic cross-sections discussed earlier. In a second set of runs, the fractionation effects of the destruction rates of N2O by O(1D) are added to the model. The second set of runs will be our standard case for the rest of the paper.

4. Results and Discussions

4.1. The Most Abundant Isotopologue 14N14N16O

A first test of the validity of our model is a comparison of the mixing ratio of N2O predicted by the model with...
noticable discrepancy between the model and observation at very high altitudes (<1 mbar pressure). However, there is great uncertainty in the measurements in this region, and the discrepancy does not imply model deficiencies. The model 2-D mixing ratios are generally in agreement with previous studies [e.g., Proffitt et al., 1992].

4.2. Isotopic Fractionation in the Stratosphere

[20] The second test of the validity of the model is the comparison between calculated enrichment values and those observed in the stratosphere. For our model, $f$ is calculated relative to a standard mixing ratio for N$_2$O of 3.1 x 10$^{-17}$ at the surface. The contribution by radiation to the fractionation factor for isotopologue or isotopomer ($i$) is given by $(\alpha_i - 1)$, where $\alpha_i$ is the ratio between $J_i$ and $J_446$. Figure 3a shows a plot of $(\alpha_i - 1)$ versus $ln\ f$ for the model using the cross-sections computed by Blake et al. [2003]. These data were from May at 35°N, corresponding to the observations of Toyoda et al. [2001]. This plot shows that the contribution by radiation to fractionation is fairly constant over a large range of N$_2$O concentrations. Figure 3b shows a plot of $ln(1 + \delta)$ versus $ln\ f$ for the model using the same cross-sections at the same latitude and month. In this plot there are two domains of linearity, each with different slopes. The first domain corresponds to the lower stratosphere below roughly 27 km, where $ln\ f$ ranges from $-0.04$ to $-0.6$. The second corresponds to the upper stratosphere between roughly 27 and 50 km; the $ln\ f$ for this domain ranges from $-0.6$ to $-4.0$. These domains of linearity in the model are also present in the observations of Röckmann et al. [2001] and Toyoda et al. [2001].

[21] For each isotopologue or isotopomer, the enrichment $\epsilon_i$ can be determined by calculating a least squares fit either to the model data or to the observations. Model results are averaged over the time periods and latitude bands corresponding to the observations and reported in Table 1. They are also averaged over the last five years of the model run, the period of time when the model should reach steady state. An example of the least squares fit is shown in Figure 4. For the upper stratospheric region, the enrichment values derived from the model run, for each isotopologue and isotopomer and the average of the $^{15}$N isotopomers, are shown in Table 2, along with the observed values of Griffith et al. [2000] (and Griffith et al. update, 2003; Griffith, private communication, 2003), Röckmann et al. [2000], and Toyoda et al. [2001]. A comparison between the model enrichment, without including the O(1D) fractionation channel, and observations for the lower stratosphere is shown in Table 3. Additionally, Table 4 shows the lower stratospheric measurements including fractionation by the O(1D) loss reaction of N$_2$O. Since the data for Rahn and Wahlen [1997], Griffith et al. [2000] and Röckmann et al. [2000] were taken from five different latitude bands and months, as opposed to Toyoda et al. [2001], which was taken from a single latitude band during a single month, the data need to be weighted appropriately in order to obtain an average of all the observations. Our weighting is by number of months and latitudes in which each set of observations was taken. Tables 2–4 also include the weighted averages of the enrichment for both model and observations.

[22] The results for the YM97 cross-sections, although following the pattern of enrichments between isotopologues

Figure 1b. A summary of the various theoretical fractionation models (this work, solid line; Yung and Miller [1997], dotted line; Johnson et al. [2001], dashed line) superimposed on room temperature laboratory mass spectrometric (Rahn et al. [1998], plusses; Röckmann et al. [2000], crosses; Röckmann et al. [2001], diamonds; Kaiser et al. [2002], closed squares) and infrared spectroscopic measurements (Turatti et al. [2000], asterisks; Zhang et al. [2000], open squares) of nitrous oxide photolysis. The corresponding error bars for the measurements are over-plotted only for those with error bars greater than their symbol size. The error bars are 2$sigma$.

observations. For this purpose we use the results of the Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) campaigns [Gunson et al., 1990; Nightingale et al., 1993]. These profiles have been observed in almost all latitudinal bands for the months of March, April and November. Concentration profiles of N$_2$O were binned into 10° latitudinal bands for each month. An example of the comparison between observations and the model at 15 N for March can be seen in Figure 2 and reveals fairly good agreement. We also give the mixing ratio of N$_2$O on the $ln\ f$ scale in this figure. In the troposphere, where there is negligible loss of N$_2$O, $ln\ f$ is close to 0. For later reference, it is convenient to divide the stratosphere roughly into two regions: the lower stratosphere where $ln\ f > -0.6$, and the upper stratosphere where $ln\ f < -0.6$. There is an area of
and isotopomers, account for less than half of the enrichment seen in observations. These results are consistent with what has been measured in laboratory studies of the isotopic fractionation of N$_2$O by photolysis. Cross-sections calculated by Johnson et al. [2001] do a better job of matching observational data, with the particular exception of (546). The (456) enrichment, while closer to observation, is still below the range of the error bars of the observations. The enrichments predicted using the cross-sections calculated by Blake et al. [2003] (see also Figure 1b) better match the observational data for all the isotopologues and isotopomers. However, there are major differences, namely, that Griffith et al.’s [2000] enrichments are all larger than the predicted values (although the error bars associated with these runs are large), while the enrichments observed using MS techniques are all smaller than the predicted values. The results of the model runs for the Blake et al. [2003] cross-sections agree quite well with the weighted averages of the three sets of observations.

As seen in Tables 2–4, there are discrepancies between the enrichments predicted by the model using any of the cross-section alternatives and those observed in the stratosphere. In general for the Blake et al. [2003] cross-sections, the enrichment predicted by the model are lower than FTS observations and higher than MS observations. However, the model matches the average of these observations. There are several possible reasons why these discrepancies are seen. First, the FTS method of retrieving the isotopic fractionation samples very long path lengths and a range of altitudes above the tangent point, and may be too sensitive to the larger signatures at higher altitudes, particularly for the optically thin isotopologue or isotopomer transitions. A second consideration is that the MS method samples more limited regions that are typically much lower in the stratosphere than the limb sounding techniques. Large sample volumes that are collected are often required, and provide another source of uncertainty that is difficult to quantify. The third possibility is that the model used has not done an adequate job of simulating the transport that influences the magnitude of the observed enrichments.

4.3. Impact of the Temperature-Dependent Cross Sections

In our model the cross-sections from Yung and Miller [1997] and Johnson et al. [2001] are at room temperature. The cross-sections from Blake et al. [2003] are temperature-dependent. As discussed earlier, we carried out an adjustment of the cross-sections of Blake et al. [2003] to fit the observations of Kaiser et al. [2002a]. The results for enrichments computed in the model are summarized under “Modified Blake et al. [2003]” in Tables 2 and 4 for the upper and lower stratosphere, respectively. There is little difference between “Modified Blake et al. [2003]” and “Blake et al. [2003]” for (456). This is consistent with the good agree-
ment between the model and measured temperature-dependent cross-sections. The results for (447) are also expected to be similar because there is little difference between the modified and original cross-sections. See previous section “Isotopic Fractionation of N2O: Mechanisms and Observations.” There are significant differences for the enrichment results for (546) and (448), of similar magnitude as the differences in the cross-sections. Overall, the modified Blake et al. [2003] cross-sections improve the agreement between the model and the MS data.

4.4. Impact of the O(1D) Channel

[26] In the 2-D model used for this paper, the contribution to fractionation by the O(1D) channel of N2O is minimal, even in the lower stratosphere. We calculate a contribution by the O(1D) channel to the total loss rate of N2O of around 8%, comparable to the accepted value of 10%. Kaiser et al. [2002b] have indicated that an important reference quantity in the lower stratosphere is the ratio \( \frac{\epsilon_{546}}{\epsilon_{546}} \), which they designate as \( \eta \). Table 5 shows a comparison of \( \eta \) between the three theoretical cross-sections and the average of the observations. Although \( \eta \) for YM97 falls within the error bars for the observations, this is only because the magnitude of the YM97 enrichment is very low compared to observations. The values of \( \eta \) from the theoretical cross-sections of Johnson et al. [2001] are much larger than observations; the greater value for \( \eta \) in this case is due to the very small value, compared with observations, of the enrichment for (546). The \( \eta \) values from the cross-sections of Blake et al. [2003] are larger than observations, but they fall within error bars.

Figure 3. (a) A plot of \( (\alpha_i - 1) \) versus \( \ln f \), where \( \alpha_i \) is the ratio of the J-value for isotopologue or isotopomer \( i \) over that for (446), and \( f \) is the fraction of N2O remaining. This plot is for May at 35°N using the theoretical cross-sections of Blake et al. [2003]. The symbols shown are: circles, 456; squares, 546; diamonds, 447; and crosses, 448. (b) A plot of \( \delta \) versus \( \ln f \) for May at 35°N using the theoretical cross-sections of Blake et al. [2003]. Fractionation by O(1D) is not included. The definition of \( \delta \) is given in the text. The inset shows the detail of the region \( 0.0 > \ln F > -0.6 \). The symbols shown are: circles, 456; squares, 546; diamonds, 447; and crosses, 448. The slopes of solid lines are the model enrichments (\( \epsilon \)). See Table 4.
4.5. Chemistry Versus Transport

[27] In an effort to understand more clearly the effect of both transport and radiation on the enrichment predicted by the model, it is useful to examine these effects separately. For this purpose, the model seasonal and latitudinal variations of \((c_i - 1)\) and \(c_i\) are examined. The latitudinal variations of \((c_i - 1)\) for (456) using the cross-sections of (448), (546), (456) are not included in the model. It is useful to examine these effects separately.

Table 2. Enrichment \((c_i)\) for Upper Stratosphere

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>YM97*</td>
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</tr>
<tr>
<td>456</td>
<td>−17.7 ± 0.3</td>
<td>−33.4 ± 0.5</td>
<td>−43.4 ± 1.0</td>
<td>−42.8 ± 1.0</td>
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<tr>
<td>546</td>
<td>−10.5 ± 0.2</td>
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<td>1115 ± 0.5</td>
<td>15.9 ± 0.4</td>
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<tr>
<td>N15</td>
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<td>−20.3 ± 0.3</td>
<td>−32.3 ± 0.8</td>
<td>−29.3 ± 0.7</td>
</tr>
<tr>
<td>447</td>
<td>−7.0 ± 0.1</td>
<td>−13.3 ± 0.2</td>
<td>−13.7 ± 0.3</td>
<td>−13.7 ± 0.3</td>
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<tr>
<td>448</td>
<td>−13.1 ± 0.2</td>
<td>−25.5 ± 0.4</td>
<td>−31.7 ± 0.8</td>
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<tr>
<td>High-latitude [Griffith et al., 2000]</td>
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<td>1175 ± 0.2</td>
<td>−13.0 ± 0.2</td>
</tr>
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<tr>
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<td>−11.3 ± 0.1</td>
<td>−11.3 ± 0.1</td>
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<td>448</td>
<td>−12.2 ± 0.2</td>
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<td>−26.2 ± 0.3</td>
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<tr>
<td>Röckmann et al. [2001]</td>
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<td>−17.8 ± 0.2</td>
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<tr>
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<td>448</td>
<td>−15.6 ± 0.1</td>
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<td>456</td>
<td>−17.6 ± 0.2</td>
<td>−32.7 ± 0.4</td>
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<td>1211 ± 0.3</td>
<td>−12.1 ± 0.2</td>
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<td>−25.1 ± 0.3</td>
<td>−31.9 ± 0.4</td>
<td>−27.0 ± 0.4</td>
</tr>
</tbody>
</table>

\*YM97, Yung and Miller [1997]; \(N15 = (\delta_{456} + \delta_{448})/2\).

Table 3. Enrichment \((c_i)\) for Lower Stratosphere—Fractionation By O(1D) Not Included in Model

<table>
<thead>
<tr>
<th>(c_i)</th>
<th>Johnson et al. [2001]</th>
<th>Blake et al. [2003]</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>YM97*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>456</td>
<td>−9.0 ± 0.1</td>
<td>−18.3 ± 0.2</td>
<td>−21.8 ± 0.2</td>
</tr>
<tr>
<td>447</td>
<td>−5.1 ± 0.1</td>
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<td>−10.2 ± 0.1</td>
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<tr>
<td>448</td>
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<td>−7.0 ± 0.1</td>
<td>−6.6 ± 0.1</td>
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<td></td>
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<tr>
<td>Weighted Average</td>
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<tr>
<td>456</td>
<td>−9.5 ± 0.1</td>
<td>−19.4 ± 0.2</td>
<td>−23.1 ± 0.2</td>
</tr>
<tr>
<td>456</td>
<td>−5.4 ± 0.1</td>
<td>−3.8 ± 0.1</td>
<td>−10.9 ± 0.1</td>
</tr>
<tr>
<td>N15</td>
<td>−7.5 ± 0.1</td>
<td>−11.0 ± 0.1</td>
<td>−16.0 ± 0.2</td>
</tr>
<tr>
<td>447</td>
<td>−3.5 ± 0.1</td>
<td>−7.4 ± 0.1</td>
<td>−6.9 ± 0.1</td>
</tr>
<tr>
<td>448</td>
<td>−6.7 ± 0.1</td>
<td>−14.1 ± 0.1</td>
<td>−16.0 ± 0.2</td>
</tr>
</tbody>
</table>

\*YM97, Yung and Miller [1997]; \(N15 = (\delta_{456} + \delta_{448})/2\).
Blake et al. [2003] are shown in Figure 5. The variations for the other isotopologues or isotopomers are similar to (456) except for their magnitude. The quantity \( \frac{a_i}{C0_1} \) becomes ill-defined in the polar region during local winter (July in the South, January in the North) due to the vanishing solar flux. For the purposes of this figure, all \( J_i < 10^{-10} \ \text{s}^{-1} \) are ignored. There is little variation between 50°S and 50°N regardless of the season. This is to be expected because there is little variation in the spectral distribution of the solar flux in this zonal region and between seasons. One aspect of \( \frac{a_i}{C0_1} \) that needs further explanation is its marked increase near the poles. This increase can be explained if the wavelength dependence of the solar fluxes between the tropics and the high latitudes is examined. There is more solar flux at wavelengths less than 200 nm in the tropics than in the high latitudes. The reason for this change in flux is the greater attenuation by O₂ at higher latitudes. For wavelengths greater than 200 nm, the difference in solar flux between the tropics and the high latitudes is not as great. In the shorter wavelength region, however, the fractionation constants are very low compared to longer wavelengths, and thus the rate of fractionation by photolysis will be greater near the poles than at the tropics.

Although the results obtained in this work are based on a 2-D model, we can nevertheless gain some insight into the effect of transport on \( \epsilon_i \) by considering an analytic 1-D model with transported parameterized by eddy diffusion [Kaye, 1987; Rahn et al., 1998]. See appendix B for details. The relation between \( \alpha_i \) and \( \epsilon_i \) in this simple model is given by

\[
\epsilon_i = (\alpha_i - 1)E
\]

\[
E = \frac{1}{2} \left( 1 + \sqrt{1 + \frac{r}{1 + r}} \right)
\]

where \( r = \tau_{\text{chem}}/4\tau_{\text{trans}} \) with \( \tau_{\text{chem}} \) = chemical lifetime = \( 1/J \) and \( \tau_{\text{trans}} \) = transport time. The transport time in the 1-D model is parameterized by \( H^2/K_1 \) where \( H \) is the scale height and \( K_1 \) is the eddy diffusion coefficient in the stratosphere. Note that \( K_1 \) must not be confused with the \( K_{zz} \) in equation (7). \( K_1 \) is much larger than \( K_{zz} \) because it includes, at least approximately, all transport processes by advection and diffusion. The estimates in appendix B suggest \( r = 0.38 \) and \( E = 0.76 \). The 1-D model also yields a simple relation between \( \epsilon_i \) and \( \delta T_i \), the difference in the mean lifetime between the isotopologue or isotopomer (i) and the most abundant isotopologue \( \delta T_i = -\epsilon_i \). These relations will be useful for interpreting the results from the 2-D model.

<table>
<thead>
<tr>
<th>YM97</th>
<th>Johnson et al. [2001]</th>
<th>Blake et al. [2003]</th>
<th>Observations (Weighted Average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_{\text{incl. O}^{17} \text{D}} ) channel</td>
<td>1.65 ± 0.12</td>
<td>4.64 ± 0.28</td>
<td>2.05 ± 0.08</td>
</tr>
<tr>
<td>( \eta_{\text{w/out O}^{17} \text{D}} ) channel</td>
<td>1.76 ± 0.05</td>
<td>5.10 ± 0.17</td>
<td>2.12 ± 0.08</td>
</tr>
</tbody>
</table>

Figure 5. A plot of model-determined \( \alpha_{456} - 1 \) as a function of latitude for four months: (a) January, (b) April, (c) July, and (d) October. The dashed lines are for the lower stratosphere (0.0 < \( \ln f < -0.6 \)). The solid lines placed are for the upper stratosphere (-0.6 < \( \ln f < -4.0 \)).
The model results for $\epsilon_{456}$ are presented in Figure 6. There are striking latitudinal and seasonal variations, which can be attributed to transport. These enrichments were computed using the cross-sections of Blake et al. [2003]. The variations in $\epsilon_i$ for the other isotopologues and isotopomers are also similar to those of $\epsilon_{456}$ except for their magnitudes. There is a large increase in $\epsilon_i$ in the tropics. This increase in $\epsilon_i$ reflects upwelling in the tropics. As demonstrated with our 1-D diffusion model, an increase in vertical transport results in an increase in isotopic enrichment. The width of the upwelling region also varies seasonally; it is narrowest in April and widest in October.

**4.6. $N_2O$ Production by Nonstandard Chemistry**

Zipf and Prasad [1998] presented evidence for a nonstandard source of $N_2O$ in the atmosphere via excited state chemistry. The reactions leading to the production of $N_2O$ can be schematically summarized by

$$O + O_2 + N_2 \rightarrow O_2 + N_2O$$

The quantum yield of (11) may be written as $Q = Q_{ZP} \times \beta$, where $Q_{ZP}$ was estimated using laboratory experiments and $\beta < 1$ is a further reduction factor introduced by us. A quantitative assessment of the impact of this hypothetical source of $N_2O$ was carried out with $\beta = 0.03$. See appendix C for details. The new source amounts to 1.53 Tg N yr$^{-1}$ and increases the mixing of $N_2O$ through out the atmosphere by about 10%. However, the new source also increases $\delta_{448}$ by more than 10% in the troposphere as well as the stratosphere! This is clearly a violation of the present observations because this implies a large unknown biological source of very small $\delta_{448}$. The source from nonstandard chemistry must be much smaller than that computed in our model.

**4.7. Implications for the Biosphere**

The total loss rates for the major isotopologue of $N_2O$ (molecules cm$^{-3}$s$^{-1}$) as a function of altitude and latitude for the four seasons are shown in Figure 7. The bulk of $N_2O$ destruction occurs in the mid stratosphere, and the maximum destruction rate follows the sun. The total atmosphere-integrated mass is 1489 Tg N. The annually averaged integrated loss rate is $9.2828 \times 10^{27}$ molecules s$^{-1}$, or 13.6 Tg N yr$^{-1}$. The mean lifetime for $N_2O$ is 109 yrs. These values are close to those in the literature [see, e.g., Houghton et al., 2001]. The annually averaged integrated loss rates for isotopologues (456), (546), (447) and (448) are $3.3735 \times 10^{25}$, $3.4063 \times 10^{25}$, $3.4442 \times 10^{24}$ and $1.8744 \times 10^{25}$, respectively. On a per molecule basis, the rates of destruction of the minor isotopologues are somewhat less than that for the major isotopologue. From the above we derive the relative rates for (446), (456), (546), (447) and (448) to be 1, 0.9843, 0.9949, and 0.9900, respectively. Thus the destruction of $N_2O$ in the atmosphere results in the isotopic fractionation of the minor isotopologues (456), (546), (447) and (448) by 19.4, 9.5, 5.5 and 12.0% respectively. If we do not distinguish between (456) and (546), we obtain 14.5% as the mean isotopic fractionation for the two isotopomers.
The enrichment values for whole atmosphere obtained above will be compared with previous results reported by Morgan et al. [2002] and Yung [2002]. Yung [2002] is the first to publish these quantitative results using the cross-sections of Blake et al. [2003] and an earlier version of the Caltech/JPL 2-D model. The results are summarized in Table 6. McLinden et al. [2003] obtained similar results using the cross-sections of Yung and Miller [1997] with scaling and Johnson et al. [2001] in a 3-D model. A detailed examination of Table 6 shows that the results in their second model (after adjustment for (546)) and Yung [2002] are within 1.1% for all isotopologues and isotopomers. This is a remarkable coincidence in view of the acknowledged numerical problems of the 3-D model in question (see appendix A) and the fact that we are comparing 2-D and 3-D models with very different physics. It is very important that the results of McLinden et al. [2003] be reproduced with an isentropic model with proven numerical stability and validated age of air. The new results in this paper are summarized in Table 6. The main difference between these and those of Yung [2002] is that the present model used the NCEP-derived circulation, whereas Yung [2002] used an older UARS-derived circulation. The two new results reflect the impact of the temperature dependent cross-sections measured by Kaiser et al. [2002a]. It remains a challenge for the 3-D model to reproduce these results.

The implications of these calculations for biospheric sources of N$_2$O are discussed below. From the extensive measurements available for $\delta^{18}$O and $\delta^{15}$N, mean tropospheric fractionation values of 20.7 and 7.0%, respectively, are found (KC93). Therefore to balance the budgets for the isotopic composition of N$_2$O, the $\delta^{15}$O and $\delta^{15}$N for the integrated sources must be 6.3 and $-7.9\%$, respectively.

There are fewer tropospheric measurements that distinguish between the (456) and (546) isotopomers. Yoshida and Toyoda [2000] reported a large site preference for the center $^{15}$N, $\delta_{456}^{15N} - \delta_{546}^{15N} = 18.7 \pm 2.2\%$. Since atmospheric chemistry can account for only $19.4 - 9.5 = 9.9\%$, the mean source of N$_2$O must have $\delta_{456}^{15N} - \delta_{546}^{15N} = 18.7 - 9.9 \pm 2.2\%$. From the preceding discussion of $\delta^{15}$N, we have $\delta_{456}^{15N} + \delta_{546}^{15N} = -14.5\%$. Solving these two equations, we obtain $\delta_{456}^{15N} = -2.9 \pm 1.1\%$ and $\delta_{546}^{15N} = -11.7 \pm 1.1\%$. This provides a quantitative evaluation of the isotopic composition of the integrated sources of N$_2$O. Further measurements, especially for the (447) isotopologue and

![Figure 7](image_url)

**Figure 7.** The total N$_2$O loss rate as a function of altitude and latitude, (a) January, (b) April, (c) July, and (d) October. The units are in molecules cm$^{-3}$ s$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>456</td>
<td>$-20.0$</td>
<td>$-14.2$</td>
<td>$-19.1$</td>
<td>$-20.0$</td>
</tr>
<tr>
<td>546</td>
<td>$-9.7$</td>
<td>$-8.2$</td>
<td>$-4.0$ ($-10.9$)</td>
<td>$-11.6$</td>
</tr>
<tr>
<td>447</td>
<td>$-6.3$</td>
<td>$-5.4$</td>
<td>$-7.3$</td>
<td>$-5.5$</td>
</tr>
<tr>
<td>448</td>
<td>$-14.4$</td>
<td>$-10.0$</td>
<td>$-13.9$</td>
<td>$-13.8$</td>
</tr>
</tbody>
</table>

**Table 6.** Enrichment ($\varepsilon_i$) for Whole Atmosphere
4.8. Implications for Atmospheric Measurements

Some critical aspects of the model results can be tested by atmospheric measurements. The model has two independent components, chemistry and transport. Since the chemistry is the same for all five isotopologues and isotopomers of N₂O, it is easier to get the correct chemistry relative to each other. As the chemical network becomes more precise, the measurements will be useful for refining our understanding of the transport processes, especially on seasonal and interannual timescales.

Figure 8a presents the latitudinal distributions of the mixing ratio of N₂O at 100 mbar, which is close to the pressure of the tropopause in the tropics. As discussed earlier, the air in the tropics ascends from the troposphere to the stratosphere. The tropical mixing ratio of N₂O is close to the surface value of 310 ppbv. At higher latitudes, the mixing ratio of N₂O is 20–40 ppbv less than those in the tropics because the air is returning from high altitudes where destruction of N₂O by photolysis has occurred. These results are consistent with KC93’s estimate of ~15 ppbv N₂O mixing ratio difference between the upwelling and downwelling regions at 100 mbar. The main differences between the winter and summer months in their respective hemispheres are photolysis (stronger in summer) and transport (stronger in winter). The effect of transport clearly overwhelms that of chemistry. To our knowledge, there has not been a systematic mapping of the latitudinal distribution of N₂O near the tropopause region for different seasons. Such measurements will provide further quantitative testing of the model.

Figure 8b presents the latitudinal distributions of the isotopic fractionation for N₂O isotopologues and isotopomers at 100 mbar as a function of latitude in January.

[34] Figure 8a presents the latitudinal distributions of the mixing ratio of N₂O at 100 mbar as a function of latitude for January and July.

[35] Figure 8b presents the latitudinal distributions of the isotopic fractionations of N₂O isotopologues and isotopomers at 100 mbar as a function of latitude in January.

[36] Figure 8b presents the latitudinal distributions of the isotopic fractionations of N₂O isotopologues and
regions are needed to resolve this discrepancy between KC93 and our model.

4.10. Causes for the Increase of Atmospheric N₂O

[46] As pointed out in the Introduction, the outstanding problem in N₂O is to find the causes for the increase of atmospheric N₂O by 11% since the Pre-Industrial Revolution (PIR) and by 44% from the Last Glacial Maximum (LGM) to PIR. Recently, Röckmann et al. [2003] determined the isotopic fractionation in N₂O in Antarctic firm samples. The decrease from PIR to the present are δ456 = −2.2‰, δ456 = −1.8‰, and δ448 = −1.2‰. This pattern of change suggests that enhanced biological emission associated with agriculture is a likely explanation [Rahn and Wahlen, 2000]. Additionally, there has not been a drastic climate change in the last few centuries. The causes for the low concentrations of N₂O during LGM may be more complex. Yang et al. [1996] argued that there was a major climate regime change. An enhanced Brewer-Dobson circulation could result in a faster transport of N₂O to the stratosphere and this implies a greater sink for N₂O. What would be the isotopic signature? As a concrete example, let us speculate that half of the 44% increase from LGM to PIR is due to a slowing down of the Brewer-Dobson circulation. Using the ideas outlined in this work, we estimate the following increase from LGM to PIR, δ456 = 1‰, δ456 = 0.5‰, δ447 = 0.3‰ and δ448 = 0.7‰. Note that δ456 and δ456 are different, because they bear the signature of the stratosphere. However, the numbers are smaller than those from the biological sources and are of the opposite sign. It remains a challenge to the experimentalists to extract this interesting information on longer timescales [Röckmann et al., 2003].
the transport in the upper stratosphere. New simultaneous measurements of the isotopologues and isotopomers of N2O and the age of air are needed to constrain the models. The back flux of N2O from the stratosphere to the troposphere, occurring primarily at high latitudes, is a source of heavy N2O to the troposphere. There appears to be some discrepancy in the magnitude of the isotopic source strengths, as defined by Equation (13). KC93 reported a value of 500 Tg N yr⁻¹%, which is much larger than the model prediction of 190 Tg N yr⁻¹%. Additional measurements in the lower stratosphere are needed to improve our understanding.

[45] It is shown that nonstandard sources of N2O are unlikely to exceed about 10% of the currently known sources. The cause for the increase of N2O in the atmosphere since the ice age is most likely biological emission. However, we speculate that there might be a contribution from a change in the stratospheric sink as a result of an atmospheric circulation regime shift. These two causes have distinctive isotopic signatures, especially in (456) and (546).

Appendix A: The Caltech/JPL 2-D Model

[44] The Caltech/JPL 2-D Model is a zonally averaged two-dimensional (2-D) model for trace species in the terrestrial troposphere and middle atmosphere [Shia et al., 1989]. It is derived from the Caltech/JPL 1-D Model [Allen et al., 1981]. The focus of our modeling effort is the simulation of the spatial distribution and temporal variation of chemical species in the atmosphere. Our model aims at integrating the information obtained by laboratory studies and atmospheric observations to achieve a quantitative understanding of the chemical, radiative and dynamical processes that are relevant to a realistic evaluation of human impact on the global environment. In the current operating mode it is a time dependent model of the global atmosphere in latitude and pressure, composed of four modules: the chemical module, the solar radiative module, the infrared radiative module, and the transport module.

[45] The dimensions in the model are arbitrary. The horizontal coordinate in the model is y = aθ, where a = planetary radius and θ = latitude. In this study, there are 18 latitude boxes, equally spaced from pole to pole. The vertical coordinate is log pressure, given by z = ln(10)p/p0, where H = 16 ln(10) = 6.949 km, p = pressure and p0 = surface pressure = 1000 mbar. The value for H is approximately the mean scale height of the atmosphere and yields z = 80 km for p = 0.01 mbar. For the present computations, the model has 40 layers, equally spaced from the surface to the upper boundary at 0.01 mbar. The tropopause (independent of season) is approximated by p = 100 mbar between 30°S and 30°N, p = 300 mbar poleward of 60°, and p = 200 mbar between 30° and 60°.

[46] The continuity equation

\[
\frac{\partial \chi}{\partial t} + v \frac{\partial \chi}{\partial y} + w \frac{\partial \chi}{\partial z} = \frac{1}{\cos \theta} \frac{\partial}{\partial z} \left( \cos \theta K_{yy} \frac{\partial \chi}{\partial z} \right) - \epsilon \frac{\partial}{\partial z} \left( e^{-K_{zz}} \frac{\partial \chi}{\partial z} \right) = \frac{Q}{M}
\]

(A1)

is solved for all long-lived species, where χ is the mixing ratio for the species; ξ = zH, and 5, w, Kyy and Kzz denote the horizontal velocity, vertical velocity, horizontal eddy diffusivity, and vertical eddy diffusivity, respectively. Q is the net chemical production rate and M is the number density of the ambient atmosphere. Until recently, the advection used in the model is the “residual mean circulation” derived from diabatic heating [Garcia and Solomon, 1983; Ko et al., 1985]. The horizontal eddy diffusivity, Kzz, is self-consistently computed from the momentum equation [Tung, 1982]. Kzz is an adjustable parameter in the model, but is set to a small value so that it does not play a crucial role in the transport of species in the troposphere and stratosphere. The input data used for the computation of transport fields (5, w, Kzz) are taken from UARS observations for 1992 [Eluszkiewicz et al., 1996] above 250 mbar. Below 250 mbar we adopt transport fields that have been tested using tracers in the troposphere [Brown, 1993]. The values for Kzz are taken from Summers et al. [1997]. They are not important except in the mesosphere. Recently, we added a new option to derive the 2-D advection from the National Center for Climate Prediction (NCEP) 3-D winds [Jiang et al., 2003, manuscript in preparation, 2003]. The advantages of the NCEP-derived advection are twofold. First, it unifies the troposphere transport (the Hadley circulation) and the stratospheric transport (Brewer-Dobson circulation). Second, it has the realism of assimilated data. However, the NCEP data are not accurate above 40 km, where we adopt the climatologically averaged circulation derived by Fleming et al. [2002] for the Goddard Space Flight Center (GSFC) 2-D model. There is a gradual merging of the two between 30 and 40 km.

[47] The model includes all the gas phase chemistry in the NASA recommendations for stratospheric modeling [DeMore et al., 1997]. Long-lived species are fixed at the ground at concentrations given by observations in 1986, as summarized in Table A1. The surface concentrations of species that have strong latitudinal gradients are presented in Table A2. The choice of 1986 as the “standard atmosphere” is motivated by the fact that it is often the starting point for decadal time dependent perturbation studies of the atmosphere. The model posits 2.65 ppbv of chlorine, 0.93 ppbv of fluorine and 15 pptv of bromine. All the important species in the major families are calculated individually without further approximation. These include the oxygen group (O, O’(D) and O3), the hydrogen group (H, OH, HO2, H2O2, H2), the methane group (CH3, CH3O, CH3O2, CH3OOH, HCO, H2CO, CO and CH4), the nitrogen group (N, NO, NO2, N2O5, HNO3, HO2NO2 and N2O), the chlorine group (Cl, ClO, HOCI, CIONO2, HCl, OCIO and CFCs), the bromine group (Br, Br2, BrO, CH3Br, CHF2Cl, CHFCl2, CH2F2Cl and CH2Cl2).

Table A1. Mixing Ratios of Long-Lived Species at the Surface

<table>
<thead>
<tr>
<th>Species</th>
<th>Mixing ratio</th>
<th>Species</th>
<th>Mixing Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3</td>
<td>3.0 × 10⁻⁸</td>
<td>CCl4</td>
<td>1.3 × 10⁻¹⁰</td>
</tr>
<tr>
<td>CH4</td>
<td>1.7 × 10⁻⁶</td>
<td>CFC14</td>
<td>1.4 × 10⁻¹⁰</td>
</tr>
<tr>
<td>H2</td>
<td>5.3 × 10⁻⁷</td>
<td>CF2Cl2</td>
<td>2.4 × 10⁻¹⁰</td>
</tr>
<tr>
<td>CO</td>
<td>see Table A2</td>
<td>CH2Cl2</td>
<td>1.1 × 10⁻¹⁰</td>
</tr>
<tr>
<td>N2O</td>
<td>3.1 × 10⁻³</td>
<td>see Table A2</td>
<td>1.9 × 10⁻¹₁</td>
</tr>
<tr>
<td>NO2</td>
<td>6.1 × 10⁻¹⁰</td>
<td>CF2Cl2</td>
<td>1.2 × 10⁻¹¹</td>
</tr>
<tr>
<td>CH3Cl</td>
<td>5.4 × 10⁻¹¹</td>
<td>CF2Cl2</td>
<td>5.4 × 10⁻¹¹</td>
</tr>
<tr>
<td>CH2FCl2</td>
<td>5.2 × 10⁻¹¹</td>
<td>CF2Cl2</td>
<td>1.7 × 10⁻¹²</td>
</tr>
<tr>
<td>CHF2Cl1</td>
<td>5.4 × 10⁻¹¹</td>
<td>CF2Cl2</td>
<td>2.0 × 10⁻¹²</td>
</tr>
<tr>
<td>CHF2Cl</td>
<td>see Table A2</td>
<td>CF2Cl2</td>
<td>see Table A2</td>
</tr>
</tbody>
</table>
Table A2. Mixing Ratios of Long-Lived Species at the Surface in Different Latitude Belts

<table>
<thead>
<tr>
<th>Latitude</th>
<th>CO</th>
<th>NO₂</th>
<th>CH₃Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>90S–80S</td>
<td>6.39 × 10⁻⁸</td>
<td>1.1 × 10⁻¹⁰</td>
<td>8.68 × 10⁻¹²</td>
</tr>
<tr>
<td>80S–70S</td>
<td>6.39 × 10⁻⁸</td>
<td>1.1 × 10⁻¹⁰</td>
<td>8.68 × 10⁻¹²</td>
</tr>
<tr>
<td>70S–60S</td>
<td>6.40 × 10⁻⁸</td>
<td>1.1 × 10⁻¹⁰</td>
<td>8.68 × 10⁻¹²</td>
</tr>
<tr>
<td>60S–50S</td>
<td>6.48 × 10⁻⁸</td>
<td>1.1 × 10⁻¹⁰</td>
<td>8.23 × 10⁻¹²</td>
</tr>
<tr>
<td>50S–40S</td>
<td>6.62 × 10⁻⁸</td>
<td>2.0 × 10⁻¹⁰</td>
<td>7.76 × 10⁻¹²</td>
</tr>
<tr>
<td>40S–30S</td>
<td>7.02 × 10⁻⁸</td>
<td>2.6 × 10⁻¹¹</td>
<td>7.80 × 10⁻¹²</td>
</tr>
<tr>
<td>30S–20S</td>
<td>8.03 × 10⁻⁸</td>
<td>2.6 × 10⁻¹¹</td>
<td>8.05 × 10⁻¹²</td>
</tr>
<tr>
<td>20S–10S</td>
<td>8.99 × 10⁻⁸</td>
<td>9.3 × 10⁻¹¹</td>
<td>8.30 × 10⁻¹²</td>
</tr>
<tr>
<td>10S–0S</td>
<td>1.01 × 10⁻⁷</td>
<td>1.1 × 10⁻¹⁰</td>
<td>8.85 × 10⁻¹²</td>
</tr>
<tr>
<td>0N–10N</td>
<td>1.02 × 10⁻⁷</td>
<td>3.1 × 10⁻¹⁰</td>
<td>9.44 × 10⁻¹²</td>
</tr>
<tr>
<td>10N–20N</td>
<td>1.02 × 10⁻⁷</td>
<td>3.1 × 10⁻¹⁰</td>
<td>1.00 × 10⁻¹¹</td>
</tr>
<tr>
<td>20N–30N</td>
<td>1.07 × 10⁻⁷</td>
<td>4.5 × 10⁻¹⁰</td>
<td>1.04 × 10⁻¹¹</td>
</tr>
<tr>
<td>30N–40N</td>
<td>1.18 × 10⁻⁷</td>
<td>4.8 × 10⁻¹⁰</td>
<td>1.07 × 10⁻¹¹</td>
</tr>
<tr>
<td>40N–50N</td>
<td>1.26 × 10⁻⁷</td>
<td>1.3 × 10⁻⁹</td>
<td>1.09 × 10⁻¹¹</td>
</tr>
<tr>
<td>50N–60N</td>
<td>1.29 × 10⁻⁷</td>
<td>1.3 × 10⁻⁹</td>
<td>1.14 × 10⁻¹¹</td>
</tr>
<tr>
<td>60N–70N</td>
<td>1.25 × 10⁻⁷</td>
<td>1.0 × 10⁻⁹</td>
<td>1.18 × 10⁻¹¹</td>
</tr>
<tr>
<td>70N–80N</td>
<td>1.21 × 10⁻⁷</td>
<td>1.1 × 10⁻⁹</td>
<td>1.21 × 10⁻¹¹</td>
</tr>
<tr>
<td>80N–90N</td>
<td>1.20 × 10⁻⁷</td>
<td>2.3 × 10⁻¹⁰</td>
<td>1.21 × 10⁻¹¹</td>
</tr>
</tbody>
</table>

BrONO₂, HBr, BrCl, CH₃Br and halons), and the fluorine group (F, FO, FO₂, FNO, FNO₂, COF₂, HF and CFCs). Water vapor is fixed to climatological values in the troposphere and to UARS values in the stratosphere. The numerical method used for solving (A1) in the model is that of Prather [1986]. The advantage of this numerical scheme, based on the conservation of second order moments, is that it has almost no numerical diffusion. Hence it is particularly suited for simulating chemical tracers with strong spatial gradients [Shia et al., 1990].

[48] A substantial portion of the photolysis of N₂O in the stratosphere occurs in the Schumann-Runge Bands (SRB) of O₂ (175–205 nm), where the band structure of the absorption spectrum has to be taken into account. The SRB of O₂ is also the primary spectral region in which other molecules such as H₂O, NO, HNO₃, and many CFCs photolyze in the stratosphere. To account for transmission in the SRB, we use the parameterization of Allen and Frederick [1982] derived from line-by-line radiative transfer calculations. We will briefly describe three model runs to demonstrate how the model simulates the stratosphere-troposphere exchange and the ozone layer.

[49] Simulations of CO₂ and SF₆ and comparisons with observations provide validation of the transport fields used in the 2-D model. CO₂ is released at the surface, and transported to the stratosphere, where it has no chemical sink and only a very small source from CH₄ oxidation. The annual increase of ~1.5 ppmv CO₂ per year makes this species particularly useful for calculating the mean age of stratospheric air parcels [Hall and Plumb, 1994; Hall and Waugh, 1997]. For the lower boundary concentrations, we use the data sets collected by the NOAA CMDL effort. For full description of the data, the reader is referred to http://www.cmdl.noaa.gov/ccg/. Weekly flask measurements are available at 47 remote sites from Alaska to the South Pole. We use the monthly mean data from 1984 to 1997, averaged in 10° latitude boxes. Figure A1 shows the results of the comparison between model (10 S to 10 N) and data from balloon and ER-2 aircraft measurements [Hall et al., 1999]. We used the NCEP-GSFC transport. The model age of air agrees well with the observations in the lower stratosphere, but is 0.5 to 1 year too short in the upper stratosphere. An adjustment is made to increase the transport above 30 km, and the revised results (solid line in Figure A1) are in good agreement with observations.

[50] Like CO₂, SF₆ is released at the surface and has an essentially infinite chemical lifetime in the stratosphere. SF₆ has a nearly constant annual growth rate of 8% per year [e.g., Geller et al., 1997]. Unlike CO₂, it does not have a seasonal cycle or stratospheric sources to complicate the calculation of mean age. The SF₆ model boundary con-

Figure A1. The vertical profile of the yearly averaged age of air over 10 S. to 10 N. derived from the 2-D model simulation of CO₂ (solid line) and SF₆ (dashed line). Also shown are the mean age calculated from OMS balloon measurements of CO₂ (crosses) and SF₆ (triangles) taken during February and November 1997 at 7 S., and ER-2 aircraft measurements of CO₂ (asterisks) and SF₆ (squares) at 20 km averaged over 10 S–10 N during 1992–1997 [Hall et al., 1999].
ditions are constrained by the measurements of the NOAA’s Climate Monitoring and Diagnostic Laboratory (CMDL). We ran the model from 1984 to 1997. The results for the age of air are summarized by the dashed line in Figure A1, and agree well with the observed values. The overall quality of agreement is similar to that for CO2. The small difference between the model ages of air derived from SF6 and CO2 is caused mainly by the seasonal cycle and the somewhat irregular rate of increase of the CMDL CO2 concentrations used to drive the model at the lower boundary. SF6 does not have a seasonal cycle.

The main advantage of the 2-D model over the 3-D model appears to be a stable numerical scheme [Prather, 1986; Shia et al., 1990] and the ability to fine-tune the transport in the model. This allows our model to reproduce the age of air to within the errors of the measurements, as shown in Figure A1. However, the 3-D model is rigorously based on fundamental principles. Hence there is little room for fine-tuning. In addition, the numerical scheme is less stable [Eluszkiewicz et al., 2002]. For example, McLinden et al. [2003] noted, “This latter model is known to have a somewhat stagnant upwelling in the tropical middle stratosphere which leads to unrealistically long N2O lifetimes and has been traced to GCM numerics.” To date, there is only one 3-D model that can satisfactorily reproduce the age of air in the stratosphere by using isentropic coordinates [Mahowald et al., 2002].

We carried out a simulation of stratospheric O3 using fixed boundary conditions for 1986. After six years, the concentrations are practically indistinguishable from one year to the next. Figure A2 (lower panel) shows the latitude-month variation in ozone column abundance simulated by our model. The units are Dobson Units (1 DU = 2.687 × 10^16 molecules/cm^2). The upper panel presents the mean from 1979 to 2000 measured by TOMS and EP TOMS [McPeters et al., 1998] (updates are available at http://toms.gsfc.nasa.gov). The model is able to qualitatively simulate most of the seasonal features, such as the northern spring maximum (>450 DU), as well as the minimum in the tropics (<250 DU). However, the model does not simulate the Antarctic Ozone Hole in the austral spring. The reason is that the loss of O3 there is caused by heterogeneous
chemistry on the surface of ice particles. The present model does not include heterogeneous chemistry.

Appendix B: Analytic Model for N2O Isotopic Fractionation

We consider the 1-D diffusion-limited case where the steady state continuity equation, equation (A1) in appendix A, for N2O is reduced to

\[-\frac{d}{dz} \left[ e^{-\xi} K_{zz} \frac{d\chi}{dz} \right] = \frac{Q}{M} \]

where \(\xi = z/H_o\), \(K_{zz}\) denotes the vertical eddy diffusivity, \(Q\) is the net chemical production and \(M\) is the number density of the atmosphere. For simplicity, we assume an isothermal atmosphere with constant scale height \(H_o\). The number density of the atmosphere is given by \(M(z) = M_0 \exp(-z/H_o)\).

The atmosphere consists of two layers, the troposphere ranging from the surface \((z = 0)\) to the tropopause \((z = z_1)\), and the stratosphere overlying the troposphere. The eddy diffusivity is assumed to be a step function, equal to \(K_o\) in the troposphere and \(K_1\) in the troposphere and stratosphere, respectively. Assuming, to a good approximation, that there is no source or sink for N2O in the troposphere, we have \(Q = 0\) for \(z < z_1\). In the stratosphere, the loss of N2O by photolysis is approximated by \(Q/M = -J \chi\), where \(J\) is the photodissociation coefficient.

With these assumptions the continuity equation (B1) in the troposphere is equivalent to

\[\frac{d\chi}{dz} = 0\]

where the flux is given by

\[\phi(z) = -K_o M(z) \frac{d\chi}{dz}\]

From (B2) we have \(\phi(z) = \phi_o = \text{constant}\), and solving (B3) we have

\[\chi(z) = \chi_o + \frac{\phi_o H_o}{K_o M_o} \left( 1 - e^{-z/H_o} \right) \]

where \(\chi_o\) and \(M_o\) refer to the mixing ratio of N2O and total number density at the surface, respectively. The RHS of (B4) is dominated by the constant term \(\chi_o\). The second term contributes at most a few percent near the tropopause.

In the stratosphere, the continuity equation (B1) becomes

\[\frac{d^2\chi}{dz^2} + \frac{1}{H_o} \frac{d\chi}{dz} - \frac{J}{K_1} \chi = 0\]

Seeking solutions of the type \(e^{\lambda z}\) reduces (B5) to a quadratic equation with two roots

\[\lambda_1 = \frac{1}{2H_o} \left( -\sqrt{1 + \frac{4JH_o}{K_1}} + 1 \right)\]

\[\lambda_2 = \frac{1}{2H_o} \left( \sqrt{1 + \frac{4JH_o}{K_1}} + 1 \right)\]

Requiring that the mixing ratio be bounded at \(z = \infty\) eliminates the second solution, and the physically acceptable solution is

\[\chi(z) = \chi_1 e^{-(z-z_1)/h}\]

where \(\chi_1 = \chi(z_1)\) from (B4) and

\[\frac{1}{h} = -\lambda_1 = \sqrt{\frac{J}{K_1}} \left( \sqrt{1 + r - \sqrt{r}} \right)\]

with \(r = \frac{K_1 J}{2H_o} < 1\). Equation (B6) provides the fundamental relation between the mixing ratio of N2O in the stratosphere and its photodissociation coefficient. The result appears to have been first derived by Kaye [1987]. For later applications to different isotopologues and isotopomers we need the logarithmic derivative of \(\frac{1}{h}\)

\[\frac{d\ln(1/h)}{dz} = \frac{1}{2} \left( 1 + \sqrt{1 + r + \sqrt{r}} \right)\]

Where the flux from the troposphere, \(\phi_o\), must balance the column integrated loss of N2O by photolysis in the stratosphere. We have

\[\phi_o = \int_{z_1}^\infty J \cdot n(z) dz\]

Combining (B4), (B9) and (B11), we have

\[\phi_o = \frac{M_0 \chi_o H_o e^{-z_1/H_o}}{1 + \frac{H_1 H_o}{K_o} \left( 1 - e^{-z_1/H_o} \right)}\]

The lifetime of N2O is given by

\[\tau = N/\phi_o\]

where \(N\) is the column density of N2O

\[N = \int_{0}^\infty M(z) \chi(z) dz\]

N consists of two parts: \(N_T\), the column in the troposphere and \(N_s\), the column in the stratosphere. Carrying out the appropriate integrals, we have

\[N_T = M_0 \chi_o H_o \left( 1 - e^{-z_1/H_o} \right) + \frac{\phi_0 H_o}{K_o} \left( \frac{1}{H_o} - e^{-z_1/H_o} \right)\]

\[N_s = \frac{M_0 \chi_o H_o e^{-z_1/H_o}}{1 + \frac{H_1 H_o}{K_o} \left( 1 - e^{-z_1/H_o} \right)}\]
This expression for $\varepsilon$ may be simplified using (B8) and we have for $\varepsilon$ (in per mil)

$$
\varepsilon = \frac{1}{2} (\alpha - 1) \left( 1 + \sqrt{\frac{r}{1 + r}} \right) \times 1000
$$

(B27)

$$
\varepsilon_f = (\alpha_f - 1) E
$$

(B28a)

$$
E = \frac{1}{2} \left( 1 + \sqrt{\frac{r}{1 + r}} \right)
$$

(B28b)

Special cases of (B28) with $E = 1$ and 0.5, have been obtained by Rahn and Wahlen [1997] and Rahn et al. [1998], respectively. The first limit obtains for $r \gg 1$, in a situation where transport is very rapid compared to chemical removal. Therefore the effect of transport on $\varepsilon_f$ can be ignored. The second limit corresponds to the case of very slow transport as compared to chemical removal. In this case $\varepsilon_f$ is only to half of its value as in the first case. Our estimate for $\varepsilon$ lies between the extreme values first derived by Rahn and Wahlen [1997] and Rahn et al. [1998]. Using representative values for the atmosphere, $K_1 = 3 \times 10^4 \text{cm}^2 \text{s}^{-1}$, $J = 4 \times 10^4 \text{s}^{-1}$, and $H = 7 \text{ km}$, we estimate $r = 0.38$ and $E = 0.76$. This results in a difference of about 25% between our results for the value of $\varepsilon$ and that from previous studies.

[58] For laboratory studies, transport can be assumed to be very rapid in the experimental apparatus, i.e., $E = 1$. Röckmann et al. [2001] report their enrichments as positive numbers and in both their observational and laboratory studies, since they define $\delta = (1/\alpha) - 1$. However, it should be noted that this definition of $\delta$ is inconsistent with their definition of $\varepsilon$, which they define exactly as it is defined in this paper. For consistency, their observational enrichments have been changed to negative values of the same magnitude in Tables 2–4.

[59] Let $\tau_A$ and $\tau_B$ be the mean lifetimes of isotopologues A and B averaged over the atmosphere, derived using (B17) for A and B. We can derive the approximate expression for $\delta \tau$ (in per mil)

$$
\delta \tau = \frac{\tau_B}{\tau_A} - 1 = (\alpha - 1) \frac{d \ln \tau}{d \ln J}
$$

(B29)

From (B18) and (B27) we can simplify (B29) to

$$
\delta \tau = -\varepsilon = -\frac{1}{2} (\alpha - 1) \left( 1 + \sqrt{\frac{r}{1 + r}} \right) \times 1000
$$

(B30)

Expressions (B25), (B27) and (B30) provides simple but highly accurate relations between the isotopic fraction $b(z)$, the ratio between dissociation coefficients $\alpha$ and the fractional difference in average lifetimes $\delta \tau$. These approximations are accurate to better than 1% in the context of the 1-D model.

**Appendix C: Nonstandard Chemistry for N₂O Production**

[60] Zipf and Prasad [1998] presented laboratory data in support of a nonstandard source of N₂O in the atmosphere. The reaction is initiated by the formation of an excited intermediate O₃NO⁺ via

$$
O + O_2 + M \rightarrow O_3^{NO} + M
$$

(C1)
followed by

\[ O_3^{N2O} + N_2 \rightarrow O_2 + N_2O \]  

(C2)

The net result is equivalent to

\[ O + O_2 + N_2 \rightarrow O_2 + N_2O \]  

(C3)

The authors estimated a quantum yield

\[ Q_{ZP} = 4 \times 10^{-5} \times \left[ \frac{p}{(p + a)} \right] \]  

(C4)

where \( p \) is the atmospheric pressure in mbar and \( a = 380 \) mbar. As we will show, the proposed quantum yield strongly violates the observational constraints, and therefore we reduce it by a factor \( \beta < 1 \)

\[ Q = Q_{ZP} \times \beta \]  

(C5)

The authors did not report the quantum yield for the (448) isotopologue. However, it is most likely that reaction (C1) favors the heavy ozone. Therefore we expect the quantum yield for (448) to be larger than that for (446)

\[ Q(448) = Q(446)[1 + \delta/1000] \]  

(C6)

We adopt the value \( \delta = 100 \) by analogy with the enrichment for heavy \( O_3 \) [Mauersberger et al., 1993].

[61] We carried out several model runs with \( \beta \) between 0 and 0.1. Figure C1a shows the mixing ratio of \( N_2O \) in ppbv in the atmosphere for January as computed by our standard model. Figure C1b shows the increase in the mixing ratios of \( N_2O \) due to the inclusion of the new source with \( \beta = 0.03 \). This choice of the value for \( \beta \) corresponds to a new \( N_2O \) source of 1.53 Tg N yr\(^{-1}\). The increase in \( N_2O \) mixing ratio is about 10% through the atmosphere. Figure C1c presents the isotopic fractionation of the (448) isotopologue in the standard model for January. Figure C1d presents the increase in fractionation due to the new source. The values for \( \delta_{448} \) increase by more than 10% throughout the atmosphere. Thus the new source has a very different pattern for \( \delta_{448} \) than that caused by photolysis. The reason is that the bulk of reaction (RC3) occurs below 20 km, while the bulk of photolysis occurs above 25 km, as shown in Figure 7.

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