Isotopic composition of stratospheric ozone

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Abstract

Using recently measured rates for isotopic variants of the ozone formation reaction $\mathrm{O + O_2 + M}$, we derive expressions for the enrichment of symmetric and asymmetric $^{50}\mathrm{O}_3$ and $^{49}\mathrm{O}_3$ in stratospheric ozone and calculate total enrichments of 123‰ and 107‰ for $^{50}\mathrm{O}_3$ and $^{49}\mathrm{O}_3$, respectively. We compare the calculations with measurements made with the Smithsonian Astrophysical Observatory far-infrared spectrometer during seven balloon flights which took place between 1989 and 1997. We find that the calculations are in reasonable agreement with the average observed enrichments of 102 ± 43‰ and 73 ± 60‰ for $^{50}\mathrm{O}_3$ and $^{49}\mathrm{O}_3$, respectively, where the errors indicate the estimated accuracy; we also find that our measurements are in agreement with other recent stratospheric and tropospheric measurements. Using our measurements of the enrichment of the asymmetric and symmetric forms of $^{50}\mathrm{O}_3$ and $^{49}\mathrm{O}_3$, we estimate branching ratios of 0.43 ± 0.03 and 0.46 ± 0.06 for production of the symmetric isotopomer by the reaction of ^{16}O with $^{34}\mathrm{O}_2$ and $^{33}\mathrm{O}_2$, respectively.

1. Introduction

Interest in the ^{18}O content of stratospheric ozone (O_3) was triggered by the suggestion that enhanced photolysis of $^{34}O_2$ may be an important source of O_3 in the upper stratosphere [*Cicerone and McCrumb,* 1980], although the authors pointed out that it would be difficult to observe the isotopic signature in O or O_3 since the Chapman reactions would dilute the enrichment in ^{18}O. Soon afterward, *Mauersberger* [1981] used an airborne mass spectrometer to measure the abundance of $^{50}O_3$ and found that it was enriched relative to the expected abundance by more than 40% at 32 km. Subsequent laboratory work revealed that ozone produced from molecular oxygen in an electric discharge is enhanced in both $^{50}O_3$ and $^{49}O_3$ by amounts which depend on pressure [*Heidenreich and Thiemens,* 1983].

Theoretical work later showed that photolysis of $^{34}O_2$ contributes less than 1% to production of ozone in the stratosphere [*Blake et al.,* 1984] and that exchange between O and O_2 is so rapid that the isotopic signature of the atomic oxygen source is quickly erased [*Kaye and Strobel,* 1983], making the observations of heavy ozone enrichments all the more puzzling. However, measurements of stratospheric ozone [*Irion et al.,* 1996, and references therein] and of ozone generated in the laboratory [*Mauersberger et al.,* 1993, and references therein] using a variety of techniques consistently find that ozone in both settings is enriched relative to O_2 in both ^{17}O and ^{18}O. The measurements also suggest that a mass-independent process is involved [*Mauersberger et al.,* 1993].

Recent laboratory measurements of the rate constants for all isotopic variants of the O + O_2 reaction [*Mauersberger et al.,* 1999, *Anderson et al.,* 1997] now make it possible to compare stratospheric measurements with expectations based on measured rather than estimated reaction rate constants. While the large effect of isototopic substitution on some of the measured rate constants remains unexplained, stratospheric measurements should be consistent with expectations based on laboratory measurements of the rates of the reactions known to be important unless there are significant gaps in our understanding of stratospheric ozone chemistry.

In the following sections, we derive expressions for the isotopic fractionation of stratospheric ozone based on measured rate constants. We then present remote sensing measurements, made with the Smithsonian Astrophysical Observatory far-infrared spectrometer (FIRS-2), of the abundance relative to $^{48}O_3$ of asymmetric and symmetric forms of $^{49}O_3$ and $^{50}O_3$, and compare FIRS-2 measurements with published results. Finally, we discuss FIRS-2 results in the context of theoretical expectations.

Recent measurements demonstrate that tropospheric ozone is also enriched in heavy isotopes [*Krankowsky et al.,* 1995, *Johnston and Thiemens,* 1997]. The tropospheric measurements show significant variability, indicating that local processes may be important [*Johnston and Thiemens,* 1997]. We ignore local effects (such as urban pollution and oxygen exchange between the atmosphere, ocean, and plants) when deriving the relationships in section 3., and so our results are most relevant for the stratosphere where such local effects are unlikely.

2. Isotopic Standards

The relative abundances of oxygen atoms in standard mean ocean water (SMOW), $^{16}\mathrm{O} : {}^{17}\mathrm{O} : {}^{18}\mathrm{O}$, are approximately $1 : 1/2700 : 1/500$. In this paper we consider only singly substituted isotopic variants, so that $^{33}O_2 \equiv {}^{17}O^{16}O$, $^{34}O_2 \equiv {}^{18}O^{16}O$, symmetric $^{49}O_3 \equiv {}^{16}O^{17}O^{16}O$, asymmetric $^{49}O_3 \equiv {}^{17}O^{16}O^{16}O$, symmetric $^{50}O_3 \equiv {}^{16}O^{18}O^{16}O$, and asymmetric $^{50}O_3 \equiv {}^{18}O^{16}O^{16}O$. The natural abundance of O_2 and O_3 molecules with multiple isotopic substitutions is low enough to be ignored in the present discussion.

Measurements of an isotope ratio R, such as $R = [^{50}O_3]/[^{48}O_3]$ where $[X]$ signifies the volume mixing ratio of X, are typically reported relative to a standard ratio R_0, often using δ notation:

$$\delta(‰) = 1000(R/R_0 - 1)\,.$$

Caution must be used in comparing measurements from different instruments to account for differences in the definition of standard isotope ratio.

The first stratospheric measurements of the abundance of $^{50}O_3$ relative to $^{48}O_3$ [*Mauersberger,* 1981, *Mauersberger,* 1987] were compared with laboratory measurements of $[^{50}O_3]/[^{48}O_3]$. Later stratospheric measurements based on laboratory analysis of returned samples [*Schueler et al.,* 1990] defined the standard abundance based on what would be expected statistically from the isotopic composition of atmospheric O_2. Finally, remote sensing measurements of isotope ratios are generally reported with respect to SMOW [*Irion et al.,* 1996, and references therein], and not all authors have used the same value for SMOW.

While the choice of reference standard is in some sense arbitrary, the same standard should be used when comparing different measurements. In the present work we report enrichments with respect to what is expected statistically. For $[^{50}O_3]/[^{48}O_3]$ and $[^{49}O_3]/[^{48}O_3]$ the statistical ratios are given by $1.5f_{18}$ and $1.5f_{17}$, respectively, where

$f_{18} = [^{34}O_2]/[^{32}O_2]$ and $f_{17} = [^{33}O_2]/[^{32}O_2]$. Atmospheric O_2 is enriched in ^{18}O by 23.5‰ with respect to SMOW [*Kroopnick and Craig,* 1972]; the enrichment in ^{17}O is 12.2‰ if we assume that the process giving rise to the enrichment in $^{34}O_2$ is mass-dependent [*Johnston and Thiemens,* 1997]. The $[^{18}O]/[^{16}O]$ and $[^{17}O]/[^{16}O]$ ratios in SMOW are 2.0052×10^{-3} and 3.72×10^{-4}, respectively [*Baertschi,* 1976], and so $f_{18} = 2(2.0523 \times 10^{-3})$ and $f_{17} = 2(3.76 \times 10^{-4})$. When comparing our measurements with published results, we first correct the published measurements for differences in the definition of standard isotope ratio.

3. Photochemistry of Heavy Ozone

To quantify the isotopic fractionation of ozone, we need to consider the reactions controlling exchange of oxygen atoms between ozone and molecular oxygen. In the following discussion, Q signifies heavy oxygen (either ^{17}O or ^{18}O), and O signifies ^{16}O.

We consider first the reaction cycle

$$\mathrm{O_2 + O + M \rightarrow O_3 + M}\,, \tag{1}$$

$$\mathrm{O_3} + h\nu \rightarrow \mathrm{O_2 + O}\,. \tag{2}$$

Other reactions which create atomic oxygen in the stratosphere (such as photolysis of O_2 and NO_2) contribute less than 1% to total production and thus are too slow to significantly affect isotope fractionation. This is not the case in the troposphere, where the rate of O-atom production from NO_2 photolysis is comparable to that from O_3 photolysis, and the rate of the reaction $\mathrm{NO} + \mathrm{O_3}$ can be more rapid than O_3 photolysis.

The corresponding reactions for heavy oxygen are

$$\mathrm{O_2 + Q + M \rightarrow OOQ + M}\,; \tag{3}$$

$$\mathrm{OOQ} + h\nu \rightarrow \mathrm{O_2 + Q}\,, \tag{4a}$$

$$\rightarrow \mathrm{O + OQ}\,; \tag{4b}$$

$$\mathrm{OQ + O + M \rightarrow OOQ + M}\,, \tag{5a}$$

$$\rightarrow \mathrm{OQO + M}\,; \tag{5b}$$

$$\mathrm{OQO} + h\nu \rightarrow \mathrm{O + OQ}\,. \tag{6}$$

As noted by *Kaye and Strobel* [1983], we must also consider the exchange reaction

$$\mathrm{Q + O_2 \rightleftharpoons O + OQ}\,. \tag{7}$$

Assuming that O and O_3 are in photochemical steady state (in the daytime $1/j_2 \leq 1500$ s), we equate rates of production (1) and loss (2) and solve for the concentration of O_3 to derive the relation

$$[\mathrm{O_3}] = k_1[\mathrm{O_2}][\mathrm{O}][\mathrm{M}]/j_2\,. \tag{8}$$

Similarly, by equating production and loss of OQO and OOQ we find that

$$[\mathrm{OQO}] = \beta k_5[\mathrm{OQ}][\mathrm{O}][\mathrm{M}]/j_6\,, \tag{9}$$

and

$$[\mathrm{OOQ}] = [\mathrm{M}](k_3[\mathrm{O_2}][\mathrm{Q}] + (1-\beta)k_5[\mathrm{OQ}][\mathrm{O}])/j_4\,; \tag{10}$$

where $j_4 = j_{4a} + j_{4b}$, $k_5 = k_{5a} + k_{5b}$, and $\beta = k_{5b}/k_5$.

Finally, we equate production (reaction (4a) and the reverse reaction (7_b)) and loss (reaction (3) and the forward reaction (7_f)) to derive the following expression for Q

$$[\mathrm{Q}] = \frac{k_{7b}[\mathrm{O}][\mathrm{OQ}]}{[\mathrm{O_2}](k_3[\mathrm{M}] + k_{7f})}\left(1 + \frac{\gamma j_4[\mathrm{OOQ}]}{k_{7b}[\mathrm{O}][\mathrm{OQ}]}\right)\,, \tag{11}$$

where $\gamma = j_{4a}/j_4$.

We can simplify (11) because the exchange reaction (7) is so rapid. If we assume that, within an order of magnitude, $j_4[\mathrm{OOQ}] \sim k_3[\mathrm{O}][\mathrm{OQ}][\mathrm{M}]$ (as is the case for the analogous reactions (1) and (2)), we find $j_4[\mathrm{OOQ}]/k_{7b}[\mathrm{O}][\mathrm{OQ}] \sim k_3[\mathrm{M}]/k_{7b} \sim k_3[\mathrm{M}]/0.5k_{7f}$. At room temperature, $k_3 \approx 6 \times 10^{-34}\,\mathrm{cm^6\,s^{-1}}$ [*Mauersberger et al.,* 1999, *Anderson et al.,* 1997] and $k_{7f} \approx 3 \times 10^{-12}\,\mathrm{cm^3\,s^{-1}}$ [*Anderson et al.,* 1985], and so at pressures less than 100 hPa, $k_3[\mathrm{M}]/k_{7f} < 1 \times 10^{-3}$. We conclude that under stratospheric conditions,

$$[\mathrm{Q}] = k_{7b}[\mathrm{O}][\mathrm{OQ}]/k_{7f}[\mathrm{O_2}]\,,$$

and so

$$[\mathrm{Q}]/[\mathrm{O}] = f/k_{eq}\,; \tag{12}$$

where $f = [\mathrm{OQ}]/[\mathrm{OO}]$ and $k_{eq} = k_{7f}/k_{7b}$. Thus the isotopic composition of atomic oxygen retains no memory of the chemical source, as pointed out by *Kaye and Strobel* [1983]. Note that this is not true for $\mathrm{O}(^1D)$ because the excited state does not survive the exchange reaction, which has implications for the isotopic composition of CO_2 [*Yung et al.,* 1997].

Combining (8), (9), (10), and (12), we derive the relations

$$[\mathrm{OQO}]/[\mathrm{O_3}] = f\beta k_5 j_2/k_1 j_6\,, \tag{13}$$

and

$$[\mathrm{OOQ}]/[\mathrm{O_3}] = f j_2[(1-\beta)k_5 + k_3/k_{eq}]/j_4 k_1\,. \tag{14}$$

Using the δ notation described in section 2., we define $\delta(\mathrm{OQO}) = 1000([\mathrm{OQO}]/0.5f[\mathrm{O_3}] - 1)$, $\delta(\mathrm{QOO}) = 1000([\mathrm{QOO}]/f[\mathrm{O_3}] - 1)$, and $\delta(\mathrm{Q}) = [2\delta(\mathrm{QOO}) + \delta(\mathrm{OQO})]/3$.

At room temperature the ratios k_3/k_1 and k_5/k_1 for Q = ^{18}O are 0.93 and 1.27, respectively; the corresponding ratios for Q = ^{17}O are 1.03 and 1.17, respectively [*Mauersberger et al.,* 1999, *Anderson et al.,* 1997]. The equilibrium constant k_{eq} is given by $1.94\exp(32/T)$ [*Kaye and Strobel,* 1983] and $1.97\exp(16/T)$ [*Yung et al.,* 1997] for Q = ^{18}O and ^{17}O, respectively, where T is temperature. We assume that $j_4 = j_6 = j_2$ and derive the following expressions:

$$\delta(^{16}\mathrm{O}^{18}\mathrm{O}^{16}\mathrm{O}) = 1000(2.54\beta_{18} - 1)\,, \quad (15)$$

$$\delta(^{18}\mathrm{O}^{16}\mathrm{O}^{16}\mathrm{O}) = 1000[1.27(1-\beta_{18}) - 0.583]\,, \quad (16)$$

$$\delta(^{16}\mathrm{O}^{17}\mathrm{O}^{16}\mathrm{O}) = 1000(2.34\beta_{17} - 1)\,, \quad (17)$$

$$\delta(^{17}\mathrm{O}^{16}\mathrm{O}^{16}\mathrm{O}) = 1000[1.17(1-\beta_{17}) - 0.512]\,, \quad (18)$$

where β_{17} and β_{18} are the values of β corresponding to the ratio k_{5b}/k_5 for ^{17}O and ^{18}O, respectively. In the stratosphere, based on (15)–(18), we expect that $\delta(^{18}\mathrm{O}) = 123‰$ and $\delta(^{17}\mathrm{O}) = 107‰$; note that the total isotopic enhancements do not depend on β.

We note that *Morton et al.* [1990] found that the isotopic composition of ozone which had been processed in a photolysis-recombination experiment depends on temperature and pressure. This implies that the ratios k_3/k_1 and k_5/k_1 depend on temperature and pressure and that the room temperature values used above may not be appropriate when analyzing stratospheric measurements.

4. Data Sets

There have been a number of observations of enrichments in heavy ozone since the first stratospheric measurements were made by *Mauersberger* [1981], and the results are not all in agreement. On the basis of equations (13) and (14) we would expect the variability in the isotope ratios to be small, resulting from the possible temperature and pressure dependence of the ratios k_3/k_1 and k_5/k_1. We now discuss and compare available measurements in order to determine whether the apparent variability is real or instrumental in nature. We will consider here measurements made with the FIRS-2 together with selected published results. All other available remote-sensing measurements either have low precision, suffer from large uncertainty in spectroscopic parameters, or provide estimates of total column density and not vertical profiles; a recent review is provided by *Irion et al.* [1996]. We renormalized the published isotope ratios when necessary to correct for differences in the definition of standard ratio, as described in section 2..

4.1. FIRS-2

The FIRS-2 is remote-sensing Fourier transform spectrometer which observes the thermal emission of the atmosphere [*Johnson et al.,* 1995]. It has flown from both balloon and aircraft platforms. During our most recent flight in April 1997 we measured vertical profiles for temperature, pressure, and the mixing ratios of 25 different molecules, including many isotopic variants. The mixing ratio profiles typically extend from the balloon altitude of around 37 km down to 18 km. In the present analysis we use data from seven balloon flights which took place between 1989 and 1997. The 1997 flight was at a latitude of 68°N; all other flights were at latitudes between 30° and 35°N.

The spectrometer resolution of 0.004 cm^{-1} (unapodized) is sufficient to resolve individual rotational transitions for $^{16}\mathrm{O}^{16}\mathrm{O}^{16}\mathrm{O}$, $^{17}\mathrm{O}^{16}\mathrm{O}^{16}\mathrm{O}$, $^{16}\mathrm{O}^{17}\mathrm{O}^{16}\mathrm{O}$, $^{18}\mathrm{O}^{16}\mathrm{O}^{16}\mathrm{O}$, and $^{16}\mathrm{O}^{18}\mathrm{O}^{16}\mathrm{O}$. Using rotational transitions results in smaller systematic errors than can be achieved using rovibrational transitions since rotational line intensities are calculated directly from electric dipole measurements. The estimated uncertainty in line intensity for the selected transitions is 3%. Although the dipole moment has not been measured for isotopically substituted ozone, we estimate that the effect of isotopic substitution on the projection of the dipole moment changes the intensity of the selected rotational transitions by less than 1%. Transitions for heavy ozone species are not saturated in the stratosphere and so are not affected by uncertainty in the pressure broadening coefficients. We carefully select transitions for $^{48}\mathrm{O}_3$ which are unsaturated and have low ground-state energies to minimize the effect of errors in the temperature profile. When analyzing data from the 1997 flight, we included a number of rovibrational transitions for $^{48}\mathrm{O}_3$ which improved the precision for retrievals below 25 km.

We show average profiles for each flight in Figure 1. The increase in scatter above 35 and below 25 km results from a decrease in precision at these altitudes. The scatter at all altitudes is consistent with the estimated precision, indicating that the variation seen in the profiles is not statistically significant. We also show in Figure 1 the results of averaging all flights together for each isotopomer. We show the total enrichment for $^{50}\mathrm{O}_3$ and $^{49}\mathrm{O}_3$ in Figure 1 and again in Figure 2. Over the altitude range 25–35 km the average enhancements for symmetric, asymmetric, and total $^{50}\mathrm{O}_3$ are 61 ± 18‰, 122 ± 10‰, and 102 ± 9‰, respectively, where all errors indicate the estimated precision. The average enhancements for symmetric, asymmetric, and total $^{49}\mathrm{O}_3$ are 16±76‰, 80±52‰, and 73±43‰, respectively. The total systematic error in each ratio is less

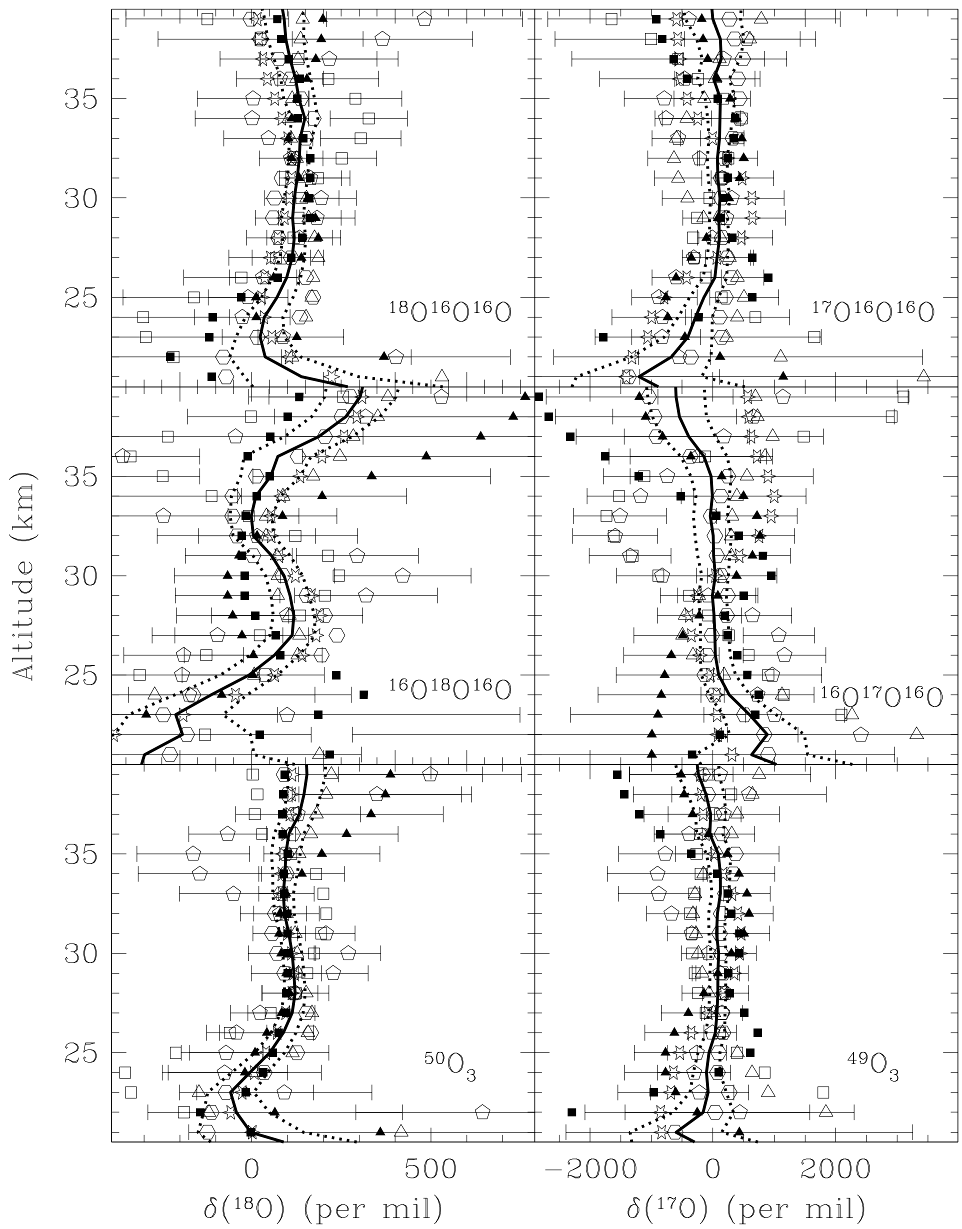

Figure 1. Ozone isotope ratios for seven balloon flights of the FIRS-2. The launch dates are September 26, 1989 (solid triangles), June 4, 1990 (open triangles), May 29, 1992 (open squares), September 29, 1992 (solid squares), March 23, 1993 (open pentagons), May 22, 1994 (open hexagons), and April 30, 1997 (stars); error bars indicate estimated precision for representative profiles. The average profile is indicated by the solid curve; dotted curves indicate estimated precision. Net enrichments for $^{50}O_3$ and $^{49}O_3$ are given by $[2\delta(QOO) + \delta(OQO)]/3$ where Q stands for ^{18}O and ^{17}O, respectively.

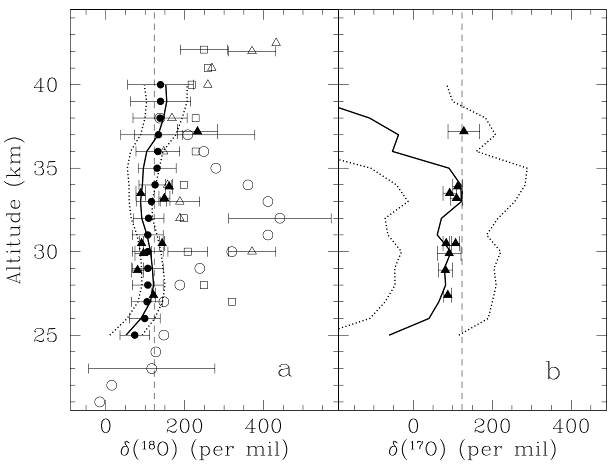

Figure 2. Comparison of FIRS-2 measurements of the enrichment in heavy ozone (solid curve) with published results; dotted curves indicate estimated precision. (a) Enrichment for $^{50}O_3$. (b) Enrichment for $^{49}O_3$. Solid circles indicates solar occultation measurements [*Irion et al.,* 1996]; solid triangles indicate results of an analysis of returned samples from four balloon flights between 1988 and 1991 [*Schueler et al.,* 1990; *Mauersberger et al.,* 1993]; measurements made during balloon flights of an in situ mass spectrometer in 1980, 1982, and 1983 [*Mauersberger,* 1981, 1987] are indicated by open circles, triangles, and squares, respectively. Dashed line indicates result of calculation described in the text.

than 42‰.

4.2. Mass Spectrometer

Mauersberger [1981] made the first measurement of stratospheric $^{50}O_3$ using an airborne mass spectrometer (AMS) and found that the ratio $[^{50}O_3]/[^{48}O_3]$ was up to 40% higher than the ratio measured in the laboratory. Later flights of the same instrument found similar enrichments, although the altitude dependence varied from flight to flight [*Mauersberger,* 1987]. The later flights also provided the first detection of $^{49}O_3$ in the stratosphere, although the measurement was used to fit the instrumental background and so did not provide an independent measurement of $[^{49}O_3]/[^{48}O_3]$. The precision of the AMS measurements is limited by counting statistics. For example, during the initial 1980 flight the total count rate (including instrumental background) for $^{50}O_3$ at 32 km was about 48 counts per 8 s measurement interval. There were typically four such measurements per kilometer during descent of the balloon. The total background was about 11 counts per 8 s at the same altitude. Count rates were higher on later flights.

The AMS measurements of $[^{50}O_3]/[^{48}O_3]$ are normalized by 1/160, the ratio measured in the laboratory [*Mauersberger,* 1981]. We have renormalized the measurements using the statistical ratio of $3(2.0523 \times 10^{-3})$ and show the results in Figure 2a. Differences between the profiles are not significant at the 95% confidence level except at 27, 30, and 32 km. The average enhancement in $^{50}O_3$ is 232 ± 12‰, and the estimated maximum systematic error is 36‰.

4.3. Cryosampler

Better precision was achieved by cryogenically collecting samples of stratospheric ozone and later analyzing the samples in the lab with the same mass spectrometer used for the AMS measurements [*Schueler et al.,* 1990, *Mauersberger et al.,* 1993]. These samples also provided the first independent measurement of $[^{49}O_3]/[^{48}O_3]$ in the stratosphere. The O_3 samples were warmed to ambient temperature and allowed to convert to O_2 over several days, and then isotope ratios in the resulting O_2 were measured. The results were reported as isotopic enrichments with respect to atmospheric O_2. We show the measurements and estimated precision in Figure 2. The average enhancements in $^{50}O_3$ and $^{49}O_3$ are 118 ± 10‰ and 95 ± 4‰, respectively; the estimated maximum systematic error is 14‰. The variability in the measurements of $^{50}O_3$ is statistically significant, while the variability in $^{49}O_3$ is not.

4.4. Solar Occultation

While a mass spectrometer offers great sensitivity, it cannot distinguish between symmetric and asymmetric forms of isotopically substituted ozone, or between different molecules having the same molecular weight. However, we note that in the middle stratosphere the volume mixing ratio of $^{50}O_3$ is of the order of 30 ppb, making it much more abundant than other naturally occurring species with the same molecular weight. Spectroscopic measurements with sufficient resolution can discriminate between different forms, but until recently such measurements have not been accurate enough to detect meaningful differences in the profiles. By averaging data obtained during four shuttle flights of the Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) solar occultation spectrometer, *Irion et al.* [1996] succeeded in measuring the first vertical profiles for both $^{16}O^{18}O^{16}O$ and $^{18}O^{16}O^{16}O$ with sufficient precision to detect a significant difference in the enrichment of the two isotopomers. The enrichments are reported with respect to a standard ratio of 2.0033×10^{-3} for $[^{18}O]/[^{16}O]$. We have renormalized the measurements using the ratio of 2.0523×10^{-3} for $[^{18}O]/[^{16}O]$; the results are shown in Figure 2a. The average enhancements for asymmetric, symmetric, and total $^{50}O_3$ are $123 \pm 60‰$, $74 \pm 70‰$, and $103 \pm 50‰$, respectively, where the errors indicate estimated precision.

Irion et al. [1996] calculated zonal averages for each of the four ATMOS missions. The zonal mean profiles for asymmetric and symmetric $^{50}O_3$ have an average precision of 80‰ and 100‰, respectively. The profiles show no statistically significant variation with latitude, altitude, or time. *Irion et al.* [1996] also presented ground-based measurements of the total column density of asymmetric $^{50}O_3$ above Table Mountain, California, covering the period 1985–1990. The individual measurements have a precision of 90‰ and show no statistically significant seasonal variation; the average column enrichment for asymmetric $^{50}O_3$ was $142 \pm 40‰$.

Interpretation of the ATMOS measurements is complicated by uncertainty in the strengths of the rovibrational transitions used for retrievals. Strengths of the $^{16}O^{18}O^{16}O$ transitions are calculated using an estimated dipole strength [*Flaud et al.,* 1986]. Strengths of the $^{18}O^{16}O^{16}O$ transitions are derived from spectroscopic measurements of a gas cell containing a mixture of $^{50}O_3$ and $^{48}O_3$ by using the calculated strengths to estimate the abundance of $^{16}O^{18}O^{16}O$ from the observed line intensities, and then assuming that $[^{18}O^{16}O^{16}O] = 2[^{16}O^{18}O^{16}O]$ [*Camy-Peyret et al.,* 1986]. This assumption may not be valid since production of the asymmetric form may be enhanced relative to the symmetric form [*Anderson et al.,* 1989].

5. Comparison Between Instruments

5.1. Enrichments

We consider first the enrichment in $^{50}O_3$, a quantity measured by all instruments described above. As shown in Figure 2a, there is good agreement among the measurements made by FIRS-2 and ATMOS and the measurements made by *Schueler et al.* [1990], while the AMS measurements show systematically larger enrichments in ^{18}O. The average difference between FIRS-2 and AMS measurements of $\delta(^{18}O)$ is 130‰, or 1.6 times the maximum combined systematic error.

The only available measurements of stratospheric $^{49}O_3$ besides those made by FIRS-2 are the cryogenic sampler (CS) measurements made by *Schueler et al.* [1990], shown in Figure 2b. Results from the two instruments are in good agreement with each other.

5.2. Variability

The AMS measurements exhibit significant variability from flight to flight and as a function of altitude. During the nighttime AMS flight in 1980, the $^{50}O_3$ signal was observed to decrease by 15% during the 2 hour float period, while the $^{48}O_3$ signal stayed constant to within 1%. This variability is difficult to understand in the context of the relationships derived in section 3.. During the day the photochemical timescale is of the order of 1500 s in the middle stratosphere, and so the isotope ratio should depend only on ambient temperature and pressure and not on the history of the air parcel. The reactions stop completely at night, which makes a 15% change even more difficult to explain.

While generally consistent with FIRS-2 and ATMOS measurements, the CS measurements of $^{50}O_3$ also show significant variability, although the amplitude is smaller than that seen by AMS. The FIRS-2 and ATMOS measurements of $^{50}O_3$ show no significant variation with altitude or time, but both data sets require averaging over many profiles to reach a meaningful level of precision, and even then the remote sensing measurements lack sufficient precision to confirm the magnitude of the variability seen by CS.

We compare the variability in CS measurements of $^{50}O_3$ and $^{49}O_3$ in Figure 3. The spread in the CS measurements of $\delta(^{18}O)$ is significantly greater than the spread in $\delta(^{17}O)$. For $\delta(^{18}O)$ the standard deviation calculated from the spread in the measurements is 46‰, while for

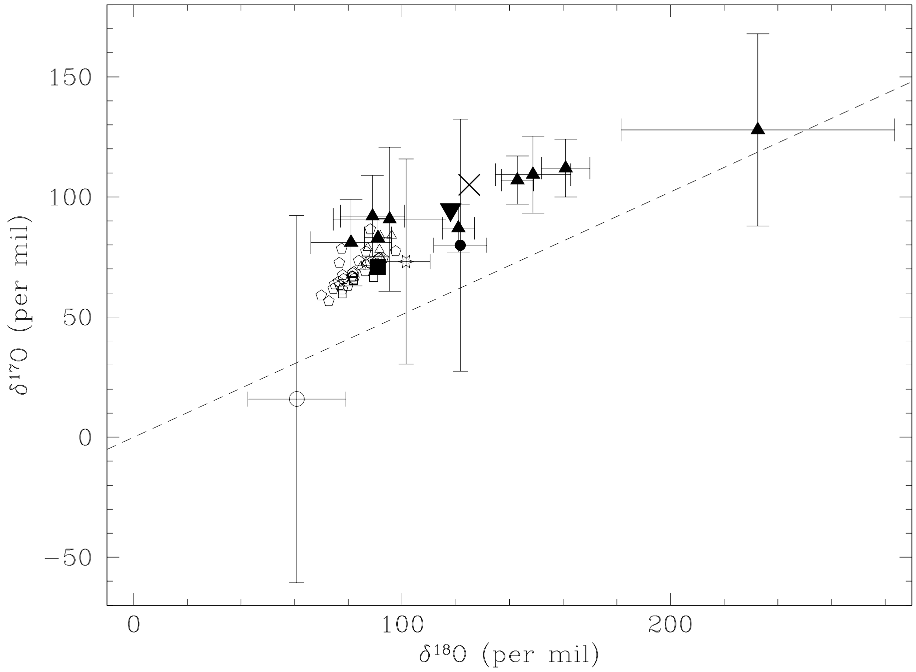

Figure 3. Three-isotope plot for ozone. We show in situ measurements for the stratosphere (solid triangles; inverted triangle indicates grand average) [*Schueler et al.,* 1990; *Mauersberger et al.,* 1993] and troposphere (solid square [*Krankowsky et al.,* 1995]; open triangles, squares, and pentagons [*Johnston and Thiemens,* 1997]), as well as FIRS-2 measurements of the symmetric (open circle), asymmetric (solid circle), and total enrichment (starred symbol); data represent the average of all measurements between 25 and 35 km. Error bars indicate estimated precision. In situ measurements do not distinguish between symmetric and asymmetric forms and measure the total enrichment only. Products of a mass-dependent fractionation process would fall on the dashed line. We also show the result of a calculation based on measured rate constants (x).

$\delta(^{17}\text{O})$ it is just 15‰ which is consistent with the measurement precision; if we ignore the CS measurement showing the largest enrichment, then the corresponding standard deviations are 29‰ and 12‰, respectively.

We also show in Figure 3 the results of mass spectrometer analysis of cryogenically collected tropospheric samples [*Krankowsky et al.,* 1995, *Johnston and Thiemens,* 1997] using different mass spectrometers than used by *Schueler et al.* [1990]. The tropospheric data are in good agreement with the average enrichments measured by FIRS-2. The standard deviation in the tropospheric measurements reported by *Johnston and Thiemens* [1997] is 6.6‰ and 6.8‰ for $\delta(^{18}\text{O})$ and $\delta(^{17}\text{O})$, respectively. The variation in $\delta(^{18}\text{O})$ and $\delta(^{17}\text{O})$ reported by *Krankowsky et al.* [1995] is similar. Overall, the variability in the troposphere is significantly smaller than that seen in the stratospheric CS measurements, whereas due to the greater influence and variability of local conditions we expect the tropospheric variability to be larger.

6. Comparison With Model

6.1. Enrichments

The FIRS-2 measurements of $\delta(^{18}\text{O})$ and $\delta(^{17}\text{O})$ are biased somewhat low with respect to the model, as shown in Figures 2 and 3. Some difference is to be expected, since equations (15)–(18) are based on room temperature measurements of the relevant rate constants at a total pressure of about 200 torr [*Mauersberger et al.,* 1999, *Anderson et al.,* 1997], and laboratory measurements have shown that enrichments in heavy ozone depend on temperature and pressure [*Morton et al.,* 1990]. The enrichment decreases with decreasing temperature and increasing pressure by roughly the right amount to account for the differences between the FIRS-2 and tropospheric measurements and the calculation shown in Figure 3.

The FIRS-2 measurements shown in Figure 3 indicate that asymmetric heavy ozone is significantly more enriched than the symmetric isotopomer. This is consistent with laboratory measurements of ozone produced in an electric discharge, which suggest that on a per molecule basis, roughly 80% of the enhancement in $^{50}\text{O}_3$ is carried by the asymmetric form [*Anderson et al.,* 1989].

We now use our measurements of symmetric and asymmetric $^{50}\text{O}_3$ and $^{49}\text{O}_3$ to estimate β_{18} and β_{17} (see equations (15)–(18)). We assume that the temperature dependence of the isotope ratio is determined by the temperature dependence of the ratio k_5/k_1. In order to reduce the effect of differences in ambient temperature we combine equations (13) and (14) and derive the following expression for β which does not depend on k_5/k_1 (again assuming that $j_4 = j_6 = j_2$):

$$\beta = \frac{\delta(\text{OQO}) + 1000}{\delta(\text{OQO}) + 1000 + 2[\delta(\text{QOO}) + 1000 - 1000k_3/k_{eq}k_1]} .$$

Using average FIRS-2 values of 60.8 ± 18.3‰, 121.7 ± 9.9‰, 15.9 ± 76.4‰, and 79.9 ± 52.5‰ for $\delta(^{16}\text{O}^{18}\text{O}^{16}\text{O})$, $\delta(^{18}\text{O}^{16}\text{O}^{16}\text{O})$, $\delta(^{16}\text{O}^{17}\text{O}^{16}\text{O})$, and $\delta(^{17}\text{O}^{16}\text{O}^{16}\text{O})$, respectively, we find that $\beta_{18} = 0.429 \pm 0.010$ and $\beta_{17} = 0.462 \pm 0.049$; the errors indicate estimated precision. The systematic error in β due to uncertainty in the line strengths is less than 6%, giving a total uncertainty of 0.028 and 0.056 for β_{18} and β_{17}, respectively.

Our estimate of β_{18} is in agreement with a previous estimate of 0.43 based on a series of laboratory measurements [*Mauersberger et al.,* 1999; *Anderson et al.,* 1997, 1989]. More recently, *Janssen et al.* [1999] measured the relative rates of reactions (5a) and (5b) in the laboratory and derived values of 1.45 ± 0.04 and 1.08 ± 0.01 for k_{5a}/k_1 and k_{5b}/k_1, respectively. Using the results of Janssen et al., we estimate that $\beta_{18} = 0.427 \pm 0.007$, in excellent agreement with the value of 0.429 ± 0.010 derived from FIRS-2 measurements.

6.2. Variability

As described above, the AMS, CS, and tropospheric measurements all display significant variability. We will limit our discussion here to variability in the stratosphere, since as described in section 3. we have not considered the effect of reactions involving NO and NO_2 which are important in the troposphere.

Possible sources of variability which were neglected in the derivation in section 3. include temperature and pressure sensitivity of the ratios k_3/k_1 and k_5/k_1; variability in the ratios j_4/j_2 and j_6/j_2; and an unknown species which exchanges oxygen atoms with O_3 at a rate comparable to O_3 photolysis. We discuss each of these in turn.

The temperature and pressure dependence of the effect of isotope substitution on reaction (1) has been explored theoretically by *Kaye* [1986] and in the laboratory by *Morton et al.* [1990]. Both studies suggest that the enhancement decreases with decreasing temperature, although the measurements show a greater temperature sensitivity than was calculated, and the theoretical study predicts an overall depletion rather than enhancement in heavy isotopes. On the basis of the measured temperature sensitivity we would expect $\delta(^{17}\text{O})$ to show 77% of the variability in $\delta(^{18}\text{O})$, rather than 33% as seen in the CS measurements.

Furthermore, assuming the temperature dependence measured by *Morton et al.* [1990], we estimate that reproducing the variation seen in the CS measurements of $\delta(^{18}\mathrm{O})$ requires changing the temperature by 153 K (or 97 K if the measurement with the largest enhancement is excluded). We conclude that temperature sensitivity is insufficient to explain the variability in the CS measurements.

We believe that variation in photolysis rates is less likely to explain variation in the isotope ratios. The rate of photolysis of O_3 changes very little with altitude between 20 and 35 km, and the effect of isotope substitution should be smaller than the effect of changing altitude over this range.

We also consider it very unlikely that there is an important exchange reaction missing from the model. The upper limit of $2 \times 10^{-25}\ \mathrm{cm}^3/\mathrm{s}$ for the rate of oxygen atom exchange between O_2 and O_3 [*Anderson et al.,* 1987] implies a time constant of 1.5×10^7s in the stratosphere, much longer than the O_3 photolysis timescale of 1500 s. The rate of $\mathrm{O_3 + NO}$ in the stratosphere is just 4% of the photolysis rate, and other reactions involving O_3 are even less important. An unknown reaction involving O_3 which is faster than $\mathrm{O_3 + NO}$ would have such a large effect on stratospheric chemistry that we doubt it could have escaped notice until now. We are left with no reasonable explanation for the variability seen in the CS measurements, or the even larger variation seen in the AMS measurements.

7. Conclusion

We believe that recent measurements of the enrichment in $^{50}\mathrm{O}_3$ and $^{49}\mathrm{O}_3$ of stratospheric ozone are in agreement with each other and with expectations based on laboratory measurements of the rates of different isotopic variants of the reaction $\mathrm{O + O_2 + M}$. We also find that formation of the asymmetric isotopomer is favored by the reaction $\mathrm{O + OQ + M}$; other laboratory studies have reached similar conclusions. The large sensitivity of the rate of the recombination reaction to isotopic composition and symmetry remains a puzzle, as does the statistically significant variability seen in mass spectrometer and cryogenic sampler measurements of the isotope ratios in the stratosphere.

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