Laboratory results from photooxidation and photolysis experiments (*17*) predict an enrichment factor of $\varepsilon = -0.6$ per mil for ^{18}O, a result which is incompatible with the value of -12.9 per mil derived from our data. If the observed stratospheric enrichments are caused by the known sink reactions, this comparison would indicate that the conditions under which the laboratory data were obtained were not representative of stratospheric conditions, and that these enrichment factors are not applicable to the stratosphere. The laboratory photolysis experiments were conducted at a wavelength of 184.9 nm, near the peak of the N_2O absorption continuum. However, peak photolysis rates in the stratosphere occur between 195 and 205 nm (*18*) because of the tail of the Schumann-Runge bands of O_2 absorption. A theoretical treatment has been carried out by Yung and Miller (*19*) which suggests the possibility of a wavelength-dependent fractionation at wavelengths greater than 185 nm. Alternatively, there may be other stratospheric sinks such as heterogeneous reactions on or in aerosols, because the samples originate from close to the Junge layer of peak concentrations of H_2SO_4 and HNO_3 aerosols (*20*). Finally, there might exist an exchange mechanism wherein isotopically enriched N and O are transferred to molecular N_2O with no apparent loss, but this is unlikely.

Thus, our data imply that the observed isotopic enrichments are the result of a stratospheric sink process and that the contribution of a return flux of isotopically enriched N_2O from the stratosphere to the troposphere should indeed help balance the isotopically light, biologically mediated, source terms as proposed by Kim and Craig (*3*) [although potential terrestrial sources of isotopically enriched N_2O have recently been observed (*21*)]. The observed enrichment factors, however, are incompatible with those produced in the laboratory and indicate that present understanding of the details of N_2O photochemistry is still incomplete.

REFERENCES AND NOTES

1. "Scientific Assessment of Ozone Depletion: 1994," *WMO Global Ozone Research and Monitoring Project–Report No. 37* (World Meteorological Organization, Geneva, Switzerland, 1995).
2. M. A. K. Khalil and R. A. Rasmussen, *J. Geophys. Res.* **97**, 14651 (1992); A. F. Bouwman, K. W. Van der Hoek, J. G. J. Olivier, *ibid.* **100**, 2785 (1995).
3. K.-R. Kim and H. Craig, *Science* **262**, 1855 (1993).
4. C. D. Keeling *et al.*, in *Aspects of Climate Variability in the Pacific and Western Americas*, D. H. Peterson, Ed. (American Geophysical Union, Washington, DC, 1989), pp. 165–236; C. M. Stevens, in *Atmospheric Methane: Sources, Sinks, and Role in Global Change*, M. A. K. Khalil, Ed. (Springer-Verlag, Berlin/Heidelberg, 1993), pp. 62–88; M. Wahlen *et al.*, *Science* **245**, 286 (1989); M. Wahlen, *Annu. Rev. Earth Planet. Sci.* **21**, 407 (1993); M. Wahlen, in *Stable Isotopes in Ecology and Environmental Science*, K. Lajtha and R. H. Michener, Eds. (Blackwell, Cambridge, MA, 1994), pp. 93–113; P. D. Quay *et al.*, *Global Biogeochem. Cycles* **5**, 25 (1991); C. M. Stevens *et al.*, *Earth Planet. Sci. Lett.* **16**, 147 (1972); M. R. Manning, C. A. M. Brenninkmeijer, W. Allan, *J. Geophys. Res.* **102**, 10673 (1997).
5. K.-R. Kim and H. Craig, *Nature* **347**, 58 (1990).
6. T. Yoshinari *et al.*, *Mar. Chem.* **56**, 253 (1997).
7. M. Wahlen and T. Yoshinari, *Nature* **313**, 780 (1985). T. Yoshinari and M. Wahlen, *ibid.* **317**, 349 (1985).
8. H. Moore, *Tellus* **26**, 169 (1974).
9. N. Yoshida, *Nature* **335**, 528 (1988); ______ and S. Matsuo, *Geochem. J.* **17**, 231 (1983).
10. $\delta = (R_s/R_{std} - 1)1000$ where R_s and R_{std} are the heavy-to-light isotope ratios in the sample and standard, respectively.
11. The mass species measured during direct injection of N_2O—44, 45, and 46 atomic mass units—are subject to interference by the abundant isotopomers of CO_2 of the same mass [N. Tanaka, D. M. Rye, R. O. Rye II, H. Avak, T. Yoshinari, *Int. J. Mass Spectrom. Ion Processes* **142**, 163 (1995); T. A. Rahn and M. Wahlen, *Eos* **77** (no. 17), S51 (1996)].
12. Purified N_2O was cryogenically separated from the air samples after removal of CO_2 with a column of ascarite. Removal of remaining contaminants was achieved by processing through a gas chromatograph fitted with a thermal conductivity detector (we used a 3/8 inch, stainless steel column of 2-m length packed with PorapakQ and operated at a temperature of 18°C with ultrahigh purity helium as carrier gas). The recovered N_2O was then measured directly by stable isotope mass spectrometry on our dual-inlet VG Prism II mass spectrometer (VG Isotech, Manchester, UK). The extraction techniques were tested with artificial air standards made with N_2O working gas of known isotopic composition. To ensure accurate isotopic analyses, we monitored two indicators of CO_2 contamination—the beam intensities of $M/z = 12$ (elemental carbon) and $M/z = 22$ (doubly ionized CO_2) {the second ionization efficiency for N_2O is negligible compared to that for CO_2 [I. Iga, M. V. V. S. Rao, S. K. Srivastrava, *J. Geophys. Res.* **101**, 9261 (1996); H. C. Straub, B. G. Lindsay, K. A. Smith, R. F. Stebbings, *J. Chem. Phys.* **105**, 4015 (1996)]}—and applied corrections when necessary. Corrections were derived from empirical relationships developed by analyses of N_2O standards spiked with known quantities of CO_2. The sensitivity of N_2O isotope analysis to CO_2 contamination in our mass spectrometer is 6.8 per mil/% CO_2 for $\delta^{15}N$ and 12.4 per mil/% CO_2 for $\delta^{18}O$. Complete removal of CO_2 has proven difficult to accomplish in the typically small sample sizes [all WB-57 samples were ~10 μl N_2O standard temperature and pressure (STP); balloon samples were ~2 μl N_2O STP]. Corrections are usually on the order of a few tenths of a per mil with corrections of several per mil not uncommon. All sample extractions and isotopic analyses were performed in November and December of 1996. Nitrous oxide mixing ratios in the samples were analyzed by a gas chromatograph with an electron capture detector immediately after collection in 1988 and 1989, and verified before extraction in 1996.
13. Atmospheric Research Equipment, Pressure System Platform, RB-57 (R)F Aircraft, *U.S. Air Force Technical Manual: T. O. 12M5-4-11-2* (1972).
14. U. Schmidt, D. Knapska, S. A. Penkett, *J. Atmos. Chem.* **3**, 363 (1985).
15. M. Wahlen *et al.*, *Eos* **70**, 1017 (1989).
16. M. B. McElroy and D. B. A. Jones, *Global Biogeochem. Cycles* **10**, 651 (1996).
17. J. Johnston, S. Cliff, M. H. Thiemens, *J. Geophys. Res.* **100**, 16801 (1993).
18. L. Froidevaux and Y. L. Yung, *Geophys. Res. Lett.* **9**, 854 (1982); K. Minschwaner, R. J. Salawitch, M. B. McElroy, *J. Geophys. Res.* **98**, 10543 (1995).
19. Y. L. Yung and C. E. Miller, *Science* **278**, 1778 (1997).
20. C. E. Junge, *Air Chemistry and Radioactivity* (Academic Press, New York, 1963).
21. K. Mandernack, T. Rahn, M. Wahlen, J. Bogner, in preparation.

22. We thank H. Weyer and the WB-57 crew for the samples collected on training flights and H. U. Schmidt for the balloon samples. Partially supported by a grant from the Max-Planck Institute of Atmospheric Chemistry, Mainz, Germany. We thank P. Crutzen for this support.

28 July 1997; accepted 27 October 1997

Isotopic Fractionation of Stratospheric Nitrous Oxide

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We propose an isotopic fractionation mechanism, based on photolytic destruction, to explain the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ fractionation of stratospheric nitrous oxide (N_2O) and reconcile laboratory experiments with atmospheric observations. The theory predicts that (i) the isotopomers $^{15}N^{14}N^{16}O$ and $^{14}N^{15}N^{16}O$ have very different isotopic fractionations in the stratosphere, and (ii) laboratory photolysis experiments conducted at 205 nanometers should better simulate the observed isotopic fractionation of stratospheric N_2O. Modeling results indicate that there is no compelling reason to invoke a significant chemical source of N_2O in the middle atmosphere and that individual N_2O isotopomers might be useful tracers of stratospheric air parcel motion.

The continued increase of N_2O in the atmosphere is a serious environmental concern because it is an efficient greenhouse gas (*1*) as well as the principal source of odd nitrogen that regulates the ozone layer (*2*). Despite its importance, the N_2O budget is currently not well quantified, which makes it difficult to determine the precise source and the cause of its increase (*3*–*6*). Recent measurements of isotopic fractionation of N_2O in the stratosphere (*7*, *8*) and laboratory experiments demonstrating an apparent lack of isotopic signature in its principal loss mechanism (*9*) (photolysis) suggest that the standard atmospheric chemistry

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Table 1. Wavelength shifts in the UV absorption spectra of various N_2O isotopomers due to ZPE differences. ZPE = $1/2\ \Sigma_i g_i \nu_i$, where g_i is the degeneracy and ν_i is the vibrational frequency. Vibrational frequencies are from (*29–32*) and are rounded to the nearest 1 cm^{-1}.

Isotopomer	ZPE	Δ(ZPE)	Wavelength shift per nanometer								
446	2343.5	0	180.000	185.000	190.000	195.000	200.000	205.000	210.000	215.000	220.000
456	2304.0	−39.5	179.872	184.865	189.858	194.850	199.842	204.834	209.826	214.818	219.809
546	2321.0	−22.5	179.927	184.923	189.919	194.914	199.910	204.905	209.901	214.896	219.891
448	2316.0	−27.5	179.911	184.906	189.901	194.895	199.890	204.884	209.879	214.873	219.867
447	2328.5	−15	179.951	184.949	184.946	194.943	199.940	204.937	209.934	214.931	219.927
556	2282.0	−61.5	179.801	184.790	189.778	194.766	199.754	204.742	209.729	214.716	219.703
458	2280.5	−63	179.796	184.785	189.773	194.761	194.748	204.736	209.723	214.709	219.696
548	2292.0	−51.5	179.833	184.824	189.814	194.804	199.794	204.784	209.773	214.762	219.751

(*10*) is incomplete. To explain these observations, several authors (*11*, *12*) have proposed nonstandard reactions for producing N_2O in the middle atmosphere. These reactions have profound implications for the atmospheric budget and the growth pattern of N_2O. However, we show that the isotopic fractionation of N_2O can be explained within the standard chemistry.

About 90% of atmospheric N_2O is lost through photolysis (*13*) in the stratosphere by absorption of solar radiation in the spectral range 185 to 210 nm

$$N_2O + h\nu\ (\lambda = 185 \text{ to } 210\ \text{nm}) \rightarrow N_2\ X(^1\Sigma_g^+) + O(^1D) \qquad (1)$$

Atmospheric N_2O is also lost through a minor channel (~10%) by reaction with $O(^1D)$ to produce two NO molecules or $N_2 + O_2$. In the absence of any significant atmospheric source of N_2O, its isotopic signature is determined by biological and industrial sources (*7*, *14*). Any enhancement of the rare isotopomers in the upper atmosphere is then a consequence of the atmospheric loss mechanisms (*1*).

The N_2O absorption spectrum is continuous between 175 and 240 nm, with a maximum near 180 nm (*15–18*), although there are some diffuse vibronic features superimposed on the continuum absorption between 175 and 195 nm (*15*, *18*). Quantum yield measurements (*10*) reveal that photoexcitation into the continuum results in unit production of $N_2\ X(^1\Sigma_g^+) + O(^1D)$. Detailed photodissociation dynamics experiments (*19–22*) are consistent with dissociation via the repulsive $B(^1\Delta)$ electronic state (*23*).

We propose that enhanced photodestruction of the $^{14}N^{14}N^{16}O$ isotopomer (referred to as 446) relative to the heavy N_2O in isotopic forms affects the isotopic composition. We assume that (i) only the $X(^1\Sigma^+) \rightarrow B(^1\Delta)$ electronic transition is involved in the absorption-photodissociation process and (ii) the two electronic potential energy surfaces are invariant to isotopic substitution. For these assumptions, isotopic substitution shifts the vibrational energy levels of the $X(^1\Sigma^+)$ state without significantly altering the continuum levels of $B(^1\Delta)$. Because all the rare isotopomers of N_2O are heavier than $^{14}N^{14}N^{16}O$, the ground state zero point vibrational energies (ZPEs) of the heavy isotopomers are reduced relative to the ZPE of (446). This situation implies that the ultraviolet (UV) absorption spectra of the heavy isotopomers will be blue-shifted relative to the (446) spectrum and that the energy shift corresponds to the respective ZPE difference. The reduced ZPEs of the heavy isotopomers result in blue shifts of only 0.1 to 0.2 nm (Table 1); yet, when convoluted with the solar flux spectrum, this subtle effect predicts the enrichment of all rare isotopomers of N_2O that are consistent with atmospheric measurements (*24*).

Using the absorption cross-section shifts

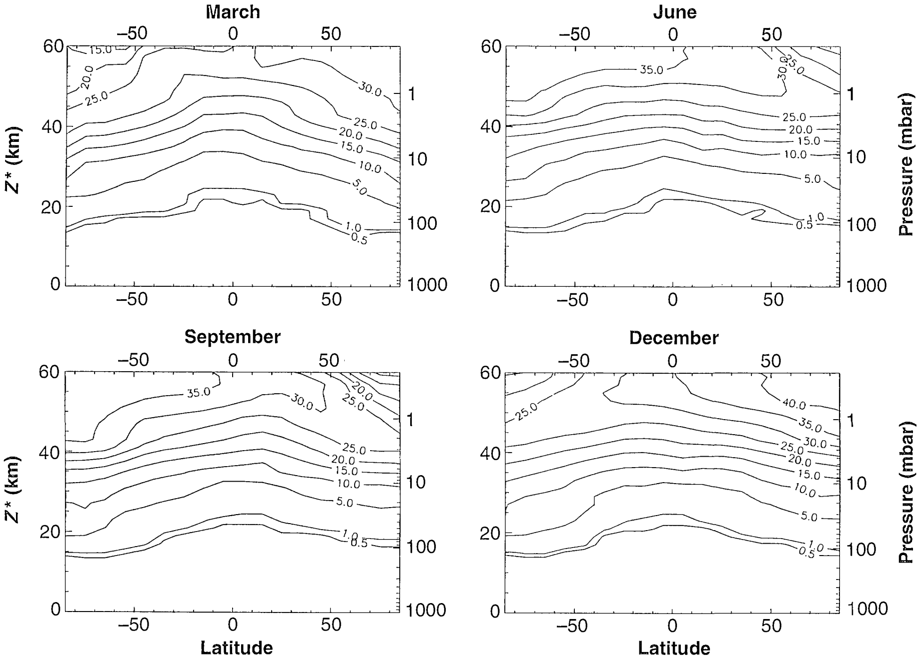

Fig. 1. Isotopic fractionation of isotopomer N_2O (448) relative to standard N_2O (446) in per mil as a function of season, latitude, and pressure. Z^* is defined by $H \log(p_0/p)$, where H = 6.949 km, p_0 = surface pressure, and p = pressure. The results were computed by standard chemical kinetics with a model of the terrestrial atmosphere (*10*). Isotopic fractionation of N_2O in the troposphere is set to zero.

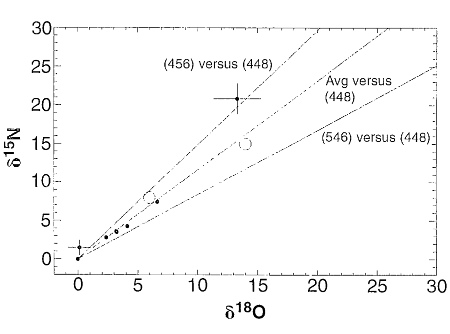

Fig. 2. Multi-isotope correlations between isotopomers of N_2O. The results for Avg were computed by using the average fractionation of (456) and (546) isotopomers, $\delta^{15}N_{ave} = (\delta^{15}N_{456} + \delta^{15}N_{546})/2$. Circles and dots are measurements of Kim and Craig (*7*) and Rahn and Wahlen (*8*), respectively. Sizes of circles represent the range of isotopic fractionation of tropospheric N_2O that has been subtracted from the data, not the errors of measurement.

calculated in Table 1, the N_2O absorption cross-section spectral function recommended by DeMore *et al.* (*10*), and a two-dimensional model of the terrestrial atmosphere (*25*), we computed the isotopic fractionation of $^{14}N^{14}N^{18}O$ (448) relative to the normal isotopomer. Enhancement of the species ($\delta^{18}O$), defined by standard convention (*8*, *14*), varies as a seasonal function of altitude and latitude (Fig. 1). Isotopic enrichment in the troposphere is set to zero. Enrichment increases in the upper stratosphere as the (446) isotopomer is preferentially photolyzed. Because the fractionation occurs only in the stratosphere, stratospheric $\delta^{18}O$ is, in general, a function of the aging of the air after it crosses the tropopause.

Our model predicts that the structural isotopomers (456) and (546) should show substantially different fractionation even though their molecular weights are identical. However, the atmospheric isotopic fractionation measurements fail to reveal this distinction because mass spectroscopic detection cannot differentiate (456) from (546) and thus lumps all $m/e = 45$ signals into a single measurement. Therefore, we expect the experimental results to coincide with a model prediction for the average $\delta^{15}N$, $\delta^{15}N_{ave} = (\delta^{15}N_{456} + \delta^{15}N_{546})/2$, and not $\delta^{15}N_{456}$ or $\delta^{15}N_{546}$ individually (see Fig. 2). The experimental data show good qualitative agreement with the model but do not provide definitive proof of its validity (*26*). In a first-order approximation, all isotopic enrichments are proportional to the magnitude of the Δ(ZPE) values listed in Table 1. Thus, we expect the largest fractionation for (556) and the least for (447). The results summarized in Fig. 2 offer an explanation for the atmospheric fractionation measurements (*7*, *8*). Furthermore, our theory reveals that the near coincidence of $\delta^{15}N$ and $\delta^{18}O$ in atmospheric N_2O is due to the inability of mass spectrometric measurements to distinguish the specific position of ^{15}N substitution in the molecule. Infrared measurements can selectively determine the atmospheric concentrations of specific isotopomers and should provide more accurate isotopic enhancement factors.

The proposed theory also explains why the recent laboratory measurements of Johnston *et al.* (*9*) failed to observe any isotopic enrichment in photolyzed $N_2{}^{16}O$, $N_2{}^{17}O$, and $N_2{}^{18}O$ samples. The reason is that the experiments were done by photodissociating N_2O at 185 nm, sampling a portion of the absorption spectrum where $d\sigma(\lambda)/d\lambda \sim 0$. Expressing the fractional change in the absorption cross section with λ as

$$F(\lambda) = \frac{1}{\sigma(\lambda)} \frac{d\sigma(\lambda)}{d\lambda} \qquad (2)$$

and using the standard recommended values (*10*), one obtains $F(185 \text{ nm}) = -0.007$ per nanometer and $F(205 \text{ nm}) = -0.180$ per nanometer. This means that a 0.1-nm shift in the absorption cross section at 185 nm produces an isotopic enhancement of only 0.7 per mil, whereas a 0.1-nm shift in the absorption cross section at 205 nm produces an isotopic enhancement on the order of 18 per mil. Thus, our mechanism suggests that N_2O isotopic enhancement is not sensitive to photolysis at 185 nm, but it is extremely sensitive to photolysis near 205 nm where the cross sections are changing rapidly. Most atmospheric N_2O photodestruction occurs at 205 nm because of the convolution of the N_2O absorption cross sections with the atmospheric UV transmission window (*27*). Therefore, repeating the experiments of Johnston *et al.* (*9*) with 205-nm light should produce $\delta^{15}N$ versus $\delta^{18}O$ correlations similar to those observed in the atmosphere.

In summary, we propose that the rate of stratospheric photodissociation governs the isotopic fractionation of atmospheric N_2O and that the photolysis rates for specific isotopomers depend on both the mass and the position of the substituted atom. Our theory suggests that we now have the ability to probe the middle atmosphere at a level of sensitivity where subtle details such as the ZPEs of molecules can yield measurable systematic effects. This creates the possibility that one may probe the chemistry and dynamics of the middle atmosphere by using all the N_2O isotopomers listed in Table 1 (*28*). The N_2O isotopomers are abundant (concentrations of several parts per billion by volume) and their chemistries are virtually identical so the observed fractionation is a simple function of the aging of the air parcel.

REFERENCES AND NOTES

1. L. G. Houghton *et al.*, Eds. *Intergovernmental Panel on Climate Change, Climate Change 1994, Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios* (Cambridge Univ. Press, New York, 1995).
2. World Meteorological Organization, Scientific Assessment of Ozone Depletion: 1994, World Meteorological Organization, *Global Ozone Research and Monitoring Project-Report 37* (World Meteorological Organization, Geneva, Switzerland, 1995).
3. R. J. Cicerone, *J. Geophys. Res.* **94**, 18265 (1989).
4. M. A. K. Khalil and R. A. Rasmussen, *ibid.* **97,** 14651 (1992).
5. M. H. Thiemens and W. C. Trogler, *Science* **251**, 932 (1991).
6. J. A. Kaye *et al.*, *NASA Reference Publication 1339* (NASA Office of the Mission to Planet Earth, Science Division, Washington, DC, 1994).
7. K.-R. Kim and H. Craig, *Science* **262**, 1855 (1993).
8. T. Rahn and M. Wahlen, *ibid.* **278**, 1776 (1997).
9. J. C. Johnston *et al.*, *J. Geophys. Res.* **100**, 16801 (1995).
10. W. B. DeMore *et al.*, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 11*, *JPL Publication 94-26* (Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 1996), p. 125.
11. S. Prasad, *J. Geophys. Res.* **99**, 5285 (1994).
12. M. B. McElroy and D. B. Jones, *Global Biogeochem. Cycles* **10**, 651 (1996).
13. K. R. Minschwaner *et al.*, *J. Geophys. Res.* **98**, 10543 (1993).
14. S. S. Cliff and M. H. Thiemens, *Science* **278**, 1774 (1997).
15. G. S. Selwyn and H. S. Johnston, *J. Chem. Phys.* **74**, 3791 (1981).
16. C. Hubrich and F. Stuhl, *J. Photochem.* **12**, 93 (1980).
17. F. Merienne, B. Coquart, A. Jenouvier, *Planet. Space Sci.* **38**, 617 (1990).
18. K. Yoshino, D. E. Freeman, W. H. Parkinson, *ibid.* **32**, 1219 (1984).
19. P. Felder, B.-M. Haas, J. R. Hüber, *Chem. Phys. Lett.* **186**, 177 (1991).
20. L. L. Springsteen, S. Satyapal, Y. Matsumi, L. M. Dobeck, P. L. Houston, *J. Phys. Chem.* **97**, 7239 (1993).
21. N. Shafer, K. Tonokura, Y. Matsumi, S. Tasaki, M. Kawasaki, *J. Chem. Phys.* **95**, 6218 (1991).
22. T. F. Hanisco and A. C. Kummel, *J. Phys. Chem.* **97,** 7242 (1993).
23. D. G. Hopper, *J. Chem. Phys.* **80**, 4290 (1984).
24. Selwyn and Johnston (*15*) recorded UV absorption spectra for the N_2O (456), (546), and (556) isotopomers and estimated ZPE shifts of 22.3, 7.6, and 31.1 cm^{-1}, respectively, based on frequency differences of the weak vibronic transitions. Although they argued that the vibronic bands were probably due to the $A(^1\Sigma^-) \leftarrow X(^1\Sigma^+)$ electronic transition instead of the $B(^1\Delta) \leftarrow X(^1\Sigma^+)$ electronic transition thought to be responsible for the continuum absorption, the shifts are similar to those reported in Table 1.
25. R.-L. Shia *et al.*, *J. Geophys. Res.* **94**, 18467 (1989).
26. Rahn and Wahlen (*8*) showed that all their fractionation data could be fitted by a simple Rayleigh distillation formula, with derived enrichment factors of $\varepsilon = -14.5$ and -12.9 per mil for the heavy nitrogen and oxygen isotopomers of N_2O, respectively. Using the same formula to fit our model results, we obtain the corresponding enrichment factors of -15.4 and -13.2, in agreement with experimental values.
27. A heuristic explanation of the computed isotopic fractionation is as follows. As first pointed out by M. J. Molina and F. S. Rowland [*Nature* **249**, 810 (1974); see also *Rev. Geophys. Space Phys.* **13**, 1 (1975)], photolysis in the far UV occurs in the stratosphere in the window 185 to 210 nm. The solar flux increases rapidly as a function of wavelength in the region. Convolution of the solar flux with the transmission window results in singling out the spectral interval 200 to 210 nm as having the maximum contribution to photolysis of N_2O [see Fig. 1 of L. Froidevaux and Y. L. Yung, *Geophys. Res. Lett.* **9**, 854 (1982)]. Thus, a slight shift in the cross section of N_2O would have a large impact on the photolysis rate of the molecule.
28. R. J. Cicerone and J. L. McCrumb [*Geophys. Res. Lett.* **7**, 251 (1980)] were probably the first to propose that photodissociation of isotopomers could have important atmospheric consequences. However, rapid exchange could dilute any photolytically derived isotopic fractionation. In the case of N_2O isotopomers, exchange with O atoms is potentially important, although the activation energy for the exchange reaction is probably very high. Appropriate laboratory experiments should settle this question.
29. J. Kolma, J. Kauppinen, V.-M. Horneman, *J. Mol. Spectrosc.* **101**, 278 (1983).
30. R. A. Toth, *J. Opt. Soc. Am. B* **3**, 1263 (1986).
31. ———, *ibid.* **4**, 357 (1987).
32. R. H. Norton and C. P. Rinsland, *Appl. Optics* **30**, 389 (1991).

33. We thank K. Boering, H. Craig, W. DeMore, R. Friedl, Y. Jiang, J. Kaye, T. Rahn, S. Sander, M. Thiemens, and M. Wahlen for valuable discussions and inputs. C.E.M. thanks the National Research Council for a NASA Jet Propulsion Laboratory Research Associateship. This research was supported in part by NASA grant NAG1-1806 to the California Institute of Technology.

11 August 1997; accepted 9 October 1997