Chem. Rev. **1999,** *99,* 2115–2136

Anomalous or Mass-Independent Isotope Effects

Ralph E. Weston, Jr.

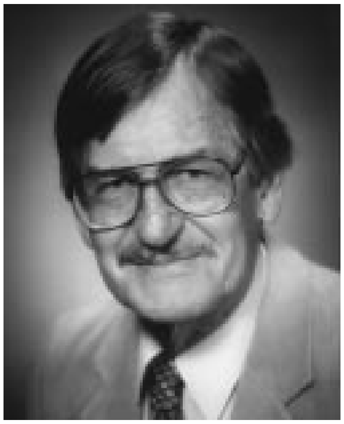
Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000

Received September 15, 1998 (Revised Manuscript Received April 26, 1999)

Contents

I. Introduction

The foundation for the quantitative understanding of isotope effects on equilibrium constants and rate constants of chemical reactions was laid about 50 years ago by Bigeleisen and Mayer,[1] Bigeleisen,[2] and Urey.[3] The paper by Urey is especially interesting in predicting the use of an isotope effect in geochemistry. He pointed out that the calculated distribution of ^{18}O between water and carbon dioxide was temperature dependent and that accurate determinations of the ^{18}O content of carbonate rocks could, therefore, be used to determine the temperature of their formation. At about the same time, Nier et al.[4] developed the dual-collector mass spectrometer, which simultaneously collects two beams of ions of different mass, thus improving the accuracy with which isotopic abundances could be compared. Further precision is obtained by sequentially comparing the sample with a standard of known isotopic composition. Isotopic ratios are typically reported in the form shown here for oxygen isotopes:



Ralph Weston received his B.S. in Chemistry from UC Berkeley and was awarded his Ph.D. by Stanford University. He was a postdoctoral fellow at Harvard University for two years before going to Brookhaven National Laboratory. Here he has spent his entire scientific career, except for two sabbaticals, one at the Centre d'Etudes Nucléaires (Saclay, France) and one at UC Berkeley. His early research focused on isotope chemistry (both the equilibria and kinetics of isotope exchange reactions) and on the use of kinetic isotope effects as a means of investigating transition states in chemical reactions. More recently, he has concentrated on laser photochemistry, using lasers both to prepare reactive species and to determine the energy distributions resulting from chemical reactions and from molecular energy transfer.

$$\delta^{18}\mathrm{O} = 10^3[(R_{\mathrm{sample}}/R_{\mathrm{standard}}) - 1], \quad \text{where } R_x = (^{18}\mathrm{O}/^{16}\mathrm{O})_x \quad (1)$$

Since this beginning about 50 years ago, theoretical approaches to the subject have become increasingly sophisticated and the experimental methods of isotope chemistry have been widely applied throughout the field of chemistry, from mechanistic studies of biochemical reactions to the determination of paleotemperatures from the isotopic composition of fossils. A large body[5−8] of both theoretical and experimental work has confirmed the basic principles set forth in the early publications. I shall refer to the type of isotope effect that has been exemplified by these theoretical and experimental studies as a "mass-dependent" effect, whether it occurs in an equilibrium or a kinetic process. As discussed in more detail below, the theory of mass-dependent isotope effects predicts that $\delta^{17}O \simeq 0.52(\delta^{18}O)$.

However, about 15 years ago, Thiemens and Heidenreich[9] reported measurements of oxygen isotope

10.1021/cr9800154 CCC: $35.00

fractionation in the formation of ozone by an electric discharge in molecular oxygen. Their surprising and unexpected finding was that the ^{18}O and ^{17}O isotopes were approximately equally enriched in the ozone product and equally depleted in the residual oxygen, contrary to the prediction of the mass-dependent model. The deviation from this model is indicated by the quantity $^{17}\Delta = \delta^{17}O - 0.52(\delta^{18}O)$. Following this initial report, a number of other reports of mass-independent isotope effects have been made, with Thiemens and co-workers being particularly active in this field. An additional reason for interest in the possibility of isotope effects not explained by the conventional mass-dependent models was provided by the observation of ^{18}O enrichment in stratospheric ozone by factors as large as 40%.[10] Subsequent work by this group and others again indicated an anomalous relationship between ^{17}O and ^{18}O effects. Concurrent with this experimental activity have been a number of attempts, in many cases by the experimentalists themselves, to provide a theoretical basis for these anomalous effects.

An example of the utility of a mass-independent isotope effect in atmospheric chemistry is provided by the recent determinations of oxygen isotope ratios in CO carried out by Huff and Thiemens.[11] First, they showed that CO in the exhaust of several motor vehicles exhibited mass-dependent isotope fractionation of oxygen, i.e., $^{17}\Delta \simeq 0$, despite a fairly wide range of 10−30‰ in $\delta^{18}O$. Air samples taken in Pasadena, an inland urban area, gave similar values. However, samples taken at several Southern California sites showed a strong inverse correlation between $^{17}\Delta$ and the CO concentration, with very high values of $^{17}\Delta$ in air samples from La Jolla, 1 km from the Pacific Ocean. This effect could be explained if the CO analyzed is the residue remaining in an air mass originally more concentrated in CO that has been undergoing a reaction with a mass-independent isotope fractionation. A strong candidate is the OH + CO sink reaction, shown to lead to large values of $^{17}\Delta$.[12] Thus, the relative value of $^{17}\Delta$ provides a sort of time and space integral of the OH concentration to which the CO in the air mass has been exposed.

Bigeleisen[13] has discussed a type of “anomalous mass effect” that is the result of nuclear field shifts and considered, in detail, the case of the U(IV)−U(VI) isotope separation. Due to differences in the size and shape of nuclei of different isotopes, there is a displacement of the ground-state electronic energy of the atom or molecule. This effect is expected to be operative only for elements near the heavy end of the periodic table and will not be discussed here.

The purpose of this paper is to review critically the literature on the subject of mass-independent isotope effects, particularly within the framework of conventional isotope effect theory. It is organized as follows: section II is a brief review of the fundamentals of mass-dependent isotope theory, particularly as it applies to heavy atoms such as oxygen. Section III describes laboratory experiments in which anomalous effects have been observed. Section IV describes measurements of oxygen isotope enrichment in tropospheric and stratospheric ozone, carbon dioxide, nitrous oxide, and carbon monoxide. Included in Sections III and IV are discussions of the various proposed theoretical explanations for the observed effects. Section V is a concluding and summarizing section.

II. Brief Summary of Isotope Effect Theory

Consider an isotope exchange equilibrium reaction of the type

$$AX_1 + BX_2 \rightleftarrows AX_2 + BX_1 \qquad (2)$$

where X_1 and X_2 represent light and heavy isotopes, respectively. The equilibrium constant can be written in terms of the partition functions, Q, of the species involved in the reaction:

$$K_{eq} = Q(AX_2)Q(BX_1)/Q(AX_1)Q(BX_2) \qquad (3)$$

Bigeleisen and Mayer[1] showed that the ratio of partition functions could be expressed entirely in terms of vibrational frequencies of the molecules reacting. They defined a function f for isotopologues by the expression

$$(s_2/s_1)f = (s_2Q_2/s_1Q_1)\prod_i(m_{1i}/m_{2i})^{3/2} = \prod_i(u_{2i}/u_{1i})\exp(\Delta u_i/2)[1 - \exp(-u_{1i})]/[1 - \exp(-u_{2i})],\ i = 1, 3n-6 \qquad (4)$$

In this expression, s_1 and s_2 are symmetry numbers, n is the number of atoms and

$$u_i = h\nu_i/k_bT,\ \Delta u_i = u_{1i} - u_{2i} \qquad (5)$$

The equilibrium constant for reaction 1 then becomes simply

$$K_{eq} = f(AX)/f(BX) \qquad (6)$$

In the case where Δu_i is small, which is the case for all isotopes except those of hydrogen, an approximate expression for $(s_2/s_1)f$ can be written:

$$(s_2/s_1)f = 1 + \sum_i G(u_i)\Delta u_i$$

$$\text{where } G(u_i) = (1/2) - (1/u_{2i}) + [\exp(u_{2i}) - 1]^{-1} \qquad (7)$$

Further approximations lead to the expression

$$(s_2/s_1)f = 1 + (1/24)(u_{1i}^{\ 2} - u_{2i}^{\ 2}) \qquad (8)$$

The magnitude of the error created by using eq 7 instead of the exact eq 4 is a function of both u_1 and Δu. Bigeleisen[14] showed that the approximation of eq 8 leads to terms of the type

$$1 + (s_2/s_1)f \approx \ln(s_2/s_1)f = (1/24)(h/k_bT)^2\sum_{i=1}^{3}(m_1^{\ -1} - m_2^{\ -1})a_{ii} + ... \qquad (9)$$

where the a_{ii} values are force constants for three orthogonal motions of the isotopically substituted atom. In this expression, all the similar terms involving atoms which do not undergo isotopic substitution have disappeared.

A comparison of two isotope effects (i.e., three isotopic species) was made for the specific case of hydrogen isotopes by Bigeleisen[15] and by Kotaka, Okamoto, and Bigeleisen.[16] The latter paper shows that anomalous mass effects can be observed at some temperatures for exchange reactions between dihydrogen and the hydrogen halides. However, these molecules differ from those containing heavier elements in having very large isotopic shifts in vibrational frequencies.

The analogous situation for the stable isotopes of oxygen was discussed by Matsuhisa et al.[17] Consider the isotopic exchange reactions

$$\mathrm{X}^{17}\mathrm{O} + \mathrm{Y}^{16}\mathrm{O} \rightleftarrows \mathrm{X}^{16}\mathrm{O} + \mathrm{Y}^{17}\mathrm{O},\ K_{17}$$

and

$$\mathrm{X}^{18}\mathrm{O} + \mathrm{Y}^{16}\mathrm{O} \rightleftarrows \mathrm{X}^{16}\mathrm{O} + \mathrm{Y}^{18}\mathrm{O},\ K_{18} \tag{10}$$

The isotopic fractionation of oxygen in these reactions is given by

$$\begin{aligned}\alpha_{17} &= ([\mathrm{Y}^{17}\mathrm{O}]/[\mathrm{Y}^{16}\mathrm{O}])/([\mathrm{X}^{17}\mathrm{O}]/[\mathrm{X}^{16}\mathrm{O}]) = K_{17}\\ &= (1 + 10^{-3}({}^{17}\delta_{\mathrm{YO}}))/(1 + 10^{-3}({}^{17}\delta_{\mathrm{XO}}))\\ \alpha_{18} &= ([\mathrm{Y}^{18}\mathrm{O}]/[\mathrm{Y}^{16}\mathrm{O}])/([\mathrm{X}^{18}\mathrm{O}]/[\mathrm{X}^{16}\mathrm{O}]) = K_{18}\\ &= (1 + 10^{-3}({}^{18}\delta_{\mathrm{YO}}))/(1 + 10^{-3}({}^{18}\delta_{\mathrm{XO}}))\end{aligned}$$

The relative fractionation of ^{18}O and ^{17}O is given by

$$\frac{\ln \alpha_{17}}{\ln \alpha_{18}} = \frac{\ln(s_2/s_1)f_{17}(\mathrm{YO}) - \ln(s_2/s_1)f_{17}(\mathrm{XO})}{\ln(s_2/s_1)f_{18}(\mathrm{YO}) - \ln(s_2/s_1)f_{18}(\mathrm{XO})} \tag{12}$$

By use of eq 9, this can be written in terms of atomic masses

$$\ln \alpha_{17}/\ln \alpha_{18} = \frac{({m_{16}}^{-1} - {m_{17}}^{-1})\sum_{i=1}^{3} a_{ii}(\mathrm{YO}) - a_{ii}(\mathrm{XO})}{({m_{16}}^{-1} - {m_{18}}^{-1})\sum_{i=1}^{3} a_{ii}(\mathrm{YO}) - a_{ii}(\mathrm{XO})} \tag{13}$$

$$= ({}^{17}\delta_{\mathrm{YO}} - {}^{17}\delta_{\mathrm{XO}})/({}^{18}\delta_{\mathrm{YO}} - {}^{18}\delta_{\mathrm{XO}}) = 0.529 \tag{14}$$

The expansion for the function $G(u)$ (eq 8) is convergent for values of u less than 2π, which is a severe limitation. However, it is important to note that the exact calculations of $(s_2/s_1)f$ by Matsuhisa et al.[17] for carbon dioxide and water containing ^{16}O, ^{17}O, and ^{18}O show that eq 14 is remarkably accurate even for values of u that are much larger than 2π. This is a result of the fact[18] that $G({}^{17}u_i) \simeq G({}^{18}u_i)$ and $({}^{16}u_i - {}^{17}u_i)/({}^{16}u_i - {}^{18}u_i) \simeq 0.522{-}0.526$.

The theory of kinetic isotope effects, i.e., the effect of isotopic substitution on reaction rate constants, can be developed in an approach parallel to that used to develop the theory of equilibrium or thermodynamic effects.[2] Without going into detail, I shall simply state that, within the framework of transition state theory, expressions analogous to those of eqs 2−6 lead to ratios of rate constants for isotopologues and isotopomers. This follows from the fact that the properties of the transition state are like those of a stable molecule except for one vibrational degree of freedom which becomes the reaction coordinate. According to transition-state theory, the rate constant for a reaction of the form

$$\mathrm{A} + \mathrm{BC} \rightarrow [\mathrm{ABC}]^{\ddagger} \rightarrow \mathrm{AB} + \mathrm{C} \tag{15}$$

is given by the expression

$$k = \kappa(k_{\mathrm{b}}T/h)({Q_{\mathrm{ABC}}}^{\ddagger}/Q_{\mathrm{A}}Q_{\mathrm{BC}})\exp(-\Delta E_0/k_{\mathrm{b}}T) \tag{16}$$

In this expression, κ is a transmission coefficient, k_{b} is Boltzmann's constant, T is the temperature, h is Planck's constant, the Q values are partition functions, and ΔE_0 is the activation energy at absolute zero. This form of the rate constant makes it possible to derive rate constant ratios for isotopomers and isotopologues that depend on values of f for the transition state and reactants in essentially the same way as the equilibrium constant for isotopic exchange. For example, if we consider another isotopic form of the reaction above

$$\mathrm{A} + \mathrm{BC}_i \rightarrow [\mathrm{ABC}_i]^{\ddagger} \rightarrow \mathrm{AB} + \mathrm{C}_i \tag{17}$$

the ratio of rate constants becomes

$$k_i/k = [\nu^{\ddagger}(\mathrm{ABC}_i)/\nu^{\ddagger}(\mathrm{ABC})]\mathrm{f}({\mathrm{ABC}_i}^{\ddagger}/\mathrm{ABC}^{\ddagger})/f(\mathrm{BC}_i/\mathrm{BC}) \tag{18}$$

The first term is the ratio of frequencies along the reaction coordinate. The f values can be evaluated according to eq 4 or 7. The transmission coefficient κ has been omitted, as tunneling should not be important for reactions of oxygen atoms.

In the case where rate constant ratios for three isotopologues are compared, Bigeleisen[15] indicated that the ratio of the logarithms of enrichment factors for deuterium and tritium isotopes should be very nearly the same as those found for equilibrium isotope effects. We would expect this to be even more exact in the case of isotopes which differ only slightly in mass, as in the case of oxygen.

Bigeleisen and Wolfsberg[4] derived several expressions that indicate how the ratio of rate constants for isotopic species can be derived from experimental data on the isotopic abundances in the product and the remaining reactant. These expressions are particularly simple if the isotope in question is present only at the tracer level. For example, in terms of the reactant, one finds

$$(k_2/k_1) - 1 = \ln(R_{\mathrm{af}}/R_{\mathrm{a0}})/\ln(1 - f_{\mathrm{r}}) \tag{19}$$

In this expression k_1 and k_2 are the rate constants for the light and heavy isotopologues, respectively, f_{r} is the fraction reacted, and R_{a0} and R_{af} are the initial and final isotopic compositions of the reactant, defined in the case of oxygen isotopes as

$$R_a = [^{m}O^{16}O]/[^{16}O_2] = 1 + [^{m}\delta(O_2)/1000] \qquad (20)$$

where the final form of this equation results from the definition of δ. Further simplification results if the initial oxygen isotopic composition is used as the standard, so that $\delta_{a0} = 0$. Then with the further assumption that δ is very small and $\ln(1+\delta) = \delta$, the rate constant expression becomes

$$(k_2/k_1) - 1 = 10^{-3}(\delta_{af}/\ln(1 - f_r)) \qquad (21)$$

The rate constant ratio can also be calculated from a comparison of the isotopic composition of the product with that of the initial reactant, using the expression

$$(k_2/k_1) - 1 = \ln\{1 + [f_r(R_{a0} - R_{xf})/(1 - f_r)R_{a0}]\}/\ln(1 - f_r) \qquad (22)$$

where R_{xf} is now the isotope ratio for the product after the extent of reaction f_r. With the same approximations used to derive eq 21, this expression (for smaller values of f_r) reduces to

$$(k_2/k_1) - 1 = -10^{-3}\delta_{xf}\, f_r/(1 - f_r)\ln(1 - f_r)) \qquad (23)$$

The above derivations are rigorously correct only for an elementary reaction, whereas the kinetic data in much of the literature surveyed is from reactions with mechanisms that may be complex. Nevertheless, the use of these expressions at least provides a method for comparing data from different experiments, especially since the extent of reaction is different from one experiment to another.

III. Laboratory Experiments

A. Formation of Ozone by an Electric Discharge in Oxygen

Heidenreich and Thiemens[9] reported the first example of a laboratory experiment in which a mass-independent isotope effect was observed. An electric discharge in oxygen produced ozone, which was condensed out on the walls of the reaction vessel maintained at a temperature of 77 K. The isotopic compositions of the residual oxygen and the ozone product were determined, along with the extent of reaction. As in most of the experiments by Thiemens and his students and similar experiments by others, the isotopic composition of ozone was not determined directly; rather, the ozone was decomposed thermally to oxygen, which was then admitted to the mass spectrometer. Enough information is provided in the data to permit the calculation of kinetic isotope effects, using eqs 19−23. The data for the unreacted oxygen can be used with eq 21. A plot of the numerator vs the denominator is shown in Figure 1a, and the slope corresponds to a value of 1.033 for k_{18}/k_{16}, indicating that the heavier isotope is enriched in the ozone product. The magnitude of the isotope effect is not unreasonable. The surprise results if a similar plot is made for the ^{17}O data, giving exactly the same ratio of rate constants. We can also apply eq 23 to the data for the ozone product, and Figure 1b shows a plot of the numerator vs the denominator. Again, the slope corresponds to a value of 1.033 for k_{18}/k_{16}, although the scatter in the data is quite large. The consistency of these results at least provides evidence that the isotopic analyses and measurements of f_r have been done correctly. The observation that remains unexplained is the near equality of the ^{18}O and ^{17}O isotope effects.

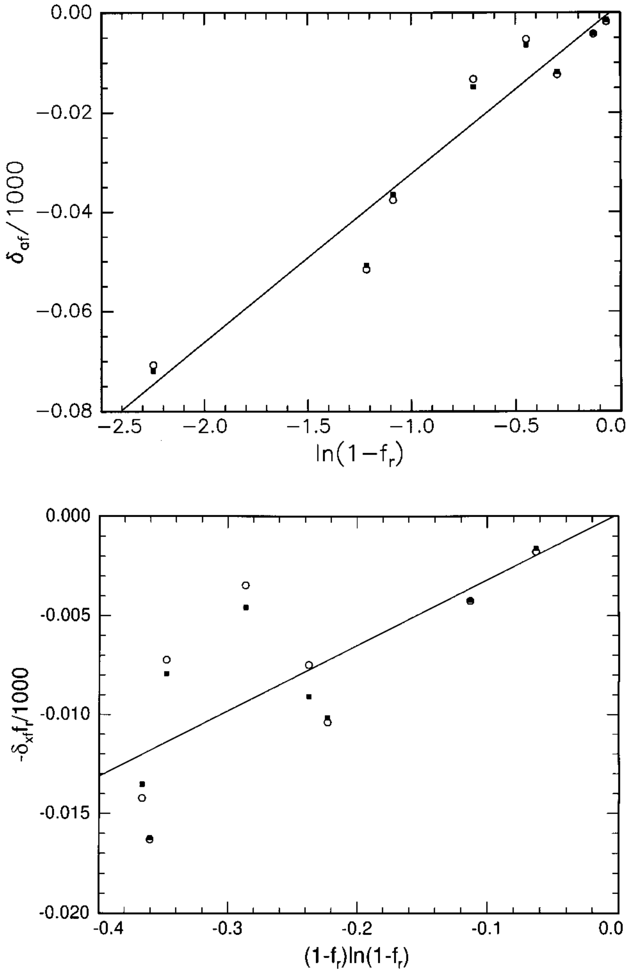


Figure 1. (a) Data of Heidenreich and Thiemens[9] for the unreacted oxygen from the production of ozone by an electric discharge, plotted according to eq 21: (○) $^{18}\delta$; (■) $^{17}\delta$. The line is the least-squares fit to the $^{18}O_2$ data with a slope $(k_{18}/k_{16}) - 1$, where the k values are rate constants for the formation of ozone. (b) Similar plot based on the data for the isotopic composition of the ozone product, plotted according to eq 23 with the numerator as the ordinate and the denominator as the abscissa. The other details are the same as in part a.

In these experiments carried out using molecular oxygen of low ^{18}O enrichment, the pertinent reactions are the following:

$$O + O_2 \rightarrow O_3 \quad k_{O+O_2} \qquad (24)$$

$$O + OQ \rightarrow OOQ/OQO \quad k_{O+OQ} \qquad (25)$$

$$Q + O_2 \rightarrow OOQ/OQO \quad k_{Q+O_2} \qquad (26)$$

where O = ^{16}O and Q = ^{17}O or ^{18}O. The rapid exchange reaction between oxygen atoms and molecules[19] leads to the condition that [Q]/[O] = [OQ]/2[O_2] ≡ R. Then the relative rates are given by

$$d([OOQ] + [OQO])/d[O_3] = (k_{O+OQ}[O][OQ] + k_{Q+O_2}[Q][O_2])/k_{O+O_2}[O][O_2] \quad (27)$$

$$d[OOQ + OQO]/d[O_3]/R = (k_{O+OQ} + k_{Q+O_2})/2k_{O+O_2} \quad (28)$$

The recent experiments of Anderson et al.[20] and Mauersberger et al.[21] lead to values of the rate constant ratios that are 1.10 for $^{17}O/^{16}O$ and 1.15 for $^{18}O/^{16}O$. These values are larger than those derived from the data of Heidenreich and Thiemens, but the latter experiments were done at room temperature rather than 77 K. This temperature dependence is in agreement with the observations of the isotope effects in the formation of ozone by photolysis of oxygen.[22]

Kaye[23] examined the kinetics of the elementary reactions involved in the equilibria of reactions 24−26. He did this by carrying out calculations of the low-pressure unimolecular dissociation constants for the various triatomic complexes. Such a rate constant could then be combined with the appropriate equilibrium constant to obtain the rate constant for the atom−molecule recombination reaction. These calculations, although not carried out using eqs 2−6, were essentially within the framework of normal mass-dependent isotope effects. Thus, it is not surprising that the rate constant ratios k_m/k_{16} differ from unity by only a few percent, nor that $[(k_{17}/k_{16}) - 1]/[(k_{18}/k_{16}) - 1]$ is about 0.5 for all the reactions considered. The authors combined their calculated rate constants with a mechanism for ozone production in an electric discharge to model the experiments of Heidenreich and Thiemens.[9] They found the calculated enhancement factors to be $^{17}\delta = -23$‰ and $^{18}\delta = -40$‰, whereas the experimental values were equal and positive, indicating enrichment of the heavy isotope in the ozone formed.

Heidenreich and Thiemens[24] later investigated the effects of pressure and the use of helium as a buffer gas. The isotopic analysis was made by comparing the isotopic ratios of the ozone formed to that of the remaining oxygen, which complicates the analysis somewhat. Equations 21 and 23 above can be combined to give

$$(k_2/k_1) - 1 = 10^{-3}(\delta_{af} - \delta_{xf})f_r/\ln(1 - f_r) \quad (29)$$

The values of the ratio of rate constants k_{18}/k_{16} calculated from their data are shown in Figure 2, from which it is seen that as the pressure increases, the ratio rises rapidly from less than unity to values comparable to those obtained in earlier work by this group. Once again, the isotopic enrichment (or depletion) in the product is essentially the same for ^{17}O and ^{18}O. The pressure effect may result from a combination of changes in the electric discharge, diffusion of ozone to the cold walls of the reactor, and collisional quenching of excited atomic or molecular states.

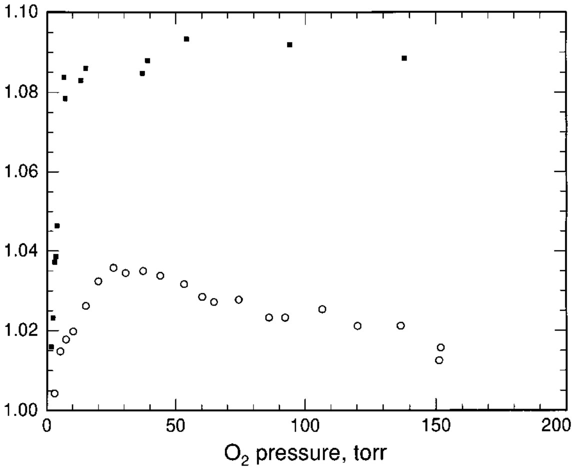


Figure 2. The rate constant ratio k_{18}/k_{16} as a function of oxygen pressure for ozone formation: (○) in an electric discharge;[24] (■) in photolysis.[43]

Bains-Sahota and Thiemens[25] changed the experiment slightly by using a microwave discharge in *flowing* oxygen at various pressures. A few experiments were also performed in which a Tesla coil discharge was used instead, both under static and flow conditions. The effect of pressure is similar to that found by Heidenreich and Thiemens,[24] although the values of δ are larger because the experiments were done at room temperature instead of 77 K. The Tesla coil discharge results are different for the static and flow conditions, with greater enrichment of the heavy isotopes in the flow system. Again, these differences may result from changes in the characteristics of the electric discharge.

Morton et al.[22] also carried out experiments in which ozone was produced by an electric discharge at various pressures. The enhancement in ozone heavy isotopes was again nearly equal for both ^{17}O and ^{18}O. The enhancement increased with pressure, in general agreement with the results of Bains-Sahota and Thiemens.[25]

The constant theme running through all the attempts to explain isotope effects that do not fit the formulations of the traditional mass-dependent effect is that of symmetry or the lack thereof. Thus, in the first laboratory exploration of the ozone formation reaction in an electric discharge, Heidenreich and Thiemens[9] propose that the reaction

$$O_2 + e^- \rightarrow O(^3P) + O(^1D) + e^- \quad (30)$$

is twice as fast for $^{17}O^{16}O$ and $^{18}O^{16}O$ as it is for $^{16}O^{16}O$ because the homonuclear molecule has only one-half as many rotational levels as the two heteronuclear molecules. It was also suggested[26] that the recombination of O and O_2 could lead to ozone in an electronically excited state that could either dissociate or drop to the ground state by photon emission. The latter process would be forbidden for certain transitions when the molecule has C_{2v} symmetry. Of course, the situation is complicated in the case of ozone, since the ^{17}O- or ^{18}O-containing molecule can have either C_{2v} or C_s symmetry. A variant of this theory[24] suggests that the nascent and vibrationally excited ozone molecule will have a longer lifetime with respect to dissociation if it is formed with an energy corresponding to an energy level of ozone near the dissociation limit. This is a process known as inverse predissociation.[27] Again, the symmetry argument indicates that the asymmetric molecule will have more rotational energy levels. This explanation would fit the observation that the isotope effects in ozone formation become smaller as the pressure increases above 1 atm,[28] making collisional energy removal and stabilization of ozone more competitive with inverse predissociation. The collisional process would not be subject to the same symmetry requirements as the inverse predissociation.

Bates[29] first applied the symmetry argument to the ozone formation reaction in a quantitative way and concluded that heavy ozone would be formed with a rate 5/3 that of the light molecule. Anderson and Kaye[30] disagreed with this analysis and pointed out that in his rate expressions, Bates had neglected isotope exchange reactions that involved the same collision complex (or activated complex) as the recombination reaction. For example,

$$\mathrm{O + OQ \rightleftarrows [OOQ]^* \rightleftarrows Q + O_2} \qquad (31)$$

where Q is either ^{17}O or ^{18}O. Bates later agreed with their analysis[31] and showed that if symmetry numbers were correctly used, no symmetry-induced isotope effect existed. In a subsequent paper, Bates[32] makes the statement “symmetry effects in association cannot in themselves cause an enhancement of the heavy ozone abundance”. This also dismisses the earlier explanation of Heidenreich and Thiemens[9] based on a symmetry effect on the density of states, since this is simply a manifestation of the general symmetry problem.

A possible way of introducing symmetry was later indicated by Bates,[32,33] who suggested that the newly formed bond of the activated complex contained more energy than the previously existing bond. Thus, in the above example

$$\mathrm{O + OQ \rightarrow O{\sim}O{-}Q^* \rightarrow O + OQ} \qquad (32)$$

or

$$\mathrm{Q + OO \rightarrow Q{\sim}O{-}O^* \rightarrow Q + OO} \qquad (33)$$

where ∼ indicates the newly formed bond. At the moment of formation, the two QOO intermediates are different and the total rate of asymmetric ozone formation will be the sum of the rates for the individual complexes. However, as energy randomization proceeds, the two complexes become more similar until finally there is only a single complex. As a result, the expected enhancement for the asymmetric molecule depends on the relative rates of energy randomization and dissociation of the complex. Reasonable rate constants for these competing processes lead to a wide range of possible enhancements. However, as pointed out by Thiemens,[34] this explanation would not account for the observed enrichment in the symmetrical isotopomer, since there are two identical ways of forming the “energetic” bond. In later paper,[33] Bates considers the enrichment of the symmetric isotopomer and suggests that it results from a “flip” in which one end breaks away from the central atom and attaches to the other end of the molecule, i.e.

$$\mathrm{O{\sim}QO \rightarrow QO{\sim}O}, \text{ etc} \qquad (34)$$

Reasonable values of the OQO/OOQ ratio are obtained if the flip frequency is the same as the dissociation frequency.

Table 1. Relative Rate Constants k_m/k_{32} for the Formation of Ozone from Oxygen in an Electric Discharge[a]

	m			
	33	34	35	36
LA series	1.022	1.021		
LM series	1.030	1.028	1.060	1.059
LE series	0.988	0.976	0.964	0.953
HA series	1.022	1.026		
HM I series	1.023	1.017	1.040	1.032
HM II series	all ratios depend on *f*			

[a] Recalculated from data in refs 35 and 36. LA and HA series: atmospheric abundance of oxygen isotopes. LM and HM I series: 1.3% ^{17}O, 2.8% ^{18}O. LE series: 38% ^{16}O, 20% ^{17}O, 42% ^{18}O. HM II series 79% ^{16}O, 6.8% ^{17}O, 14% ^{18}O.

Yang and Epstein[35,36] also carried out experiments in which ozone was produced by a microwave discharge in molecular oxygen. The isotopic compositions of the initial oxygen, the unreacted oxygen, and the oxygen formed by the complete decomposition of the ozone product were determined. In addition, oxygen highly enriched in the two heavy isotopes was used as the starting material, which made it possible to observe reactions of ^{17}O$_2$ and ^{18}O$_2$. These authors used the equivalent of eqs 19−23 to calculate rate constant ratios from values of δ, and their results are shown in Table 1. In the case of oxygen with normal isotopic composition and slightly enriched composition, the rate constant ratios are similar to those observed by Heidenreich and Thiemens and the effect of ^{17}O and ^{18}O substitution is essentially the same. Again, the effect is in the direction of enrichment of ozone in the heavier isotopic species. In the LM series, note that $[(k_{36}/k_{34}) - 1] \simeq [(k_{34}/k_{32}) - 1]$ as the analogue to eq 14 would predict. The results of the experiments with highly enriched oxygen are surprising, as the rate constant ratio has now become inverted and the ozone is depleted in the heavy isotope. Aside from this change, the results are quite self-consistent, with a constant increment in $(k_m/k_{32}) - 1$ of $0.012(32 - m)$, obeying the mass-dependent relationship.

In their second paper,[36] Yang and Epstein studied the effect of oxygen pressure and of different types of RF discharge, as well as the effect of isotopic abundance in the oxygen reactant. Again, these results are tabulated in Table 1. The samples with low abundances of the heavy isotopes (HA and HM I) give results that are in general agreement with those presented in the preceding paper. The more enriched oxygen sample produces rate constant ratios that do not obey eqs 19−23, in the sense that the rate constant ratio varies with the extent of reaction. A plot of $^{17}\delta$ against $^{18}\delta$ for most of the data reported in this and the preceding paper leads to a line with

Table 2. Isotopic Species of Ozone Produced from Highly Enriched Oxygen

		enhancement (%)				
mass	symmetric/asymmetric	ED[a]	Ph[b]	Ph[c]	Ph[d]	Rad[e]
48	16−16−16/	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
49	16−17−16/17−16−16	12.1 ± 0.2	11.3			
50	16−18−16/16−16−18	14.6 ± 0.2	13.0	21 ± 11		
50	17−16−17/16−17−17		12.1			
51	/16−17−18	20.3 ± 0.2	18.1			
51	17−17−17/		−1.8			
52	18−16−18/16−18−18	17.0 ± 0.2	14.4	15 ± 4		
52	17−18−17/18−17−17		9.5			
53	18−17−18/17−18−18	11.7 ± 0.2	8.3			
54	18−18−18/	−0.9 ± 0.2	−4.6	1 ± 8	−11.4 ± 2.4[f] (−4.6)[f]	9.8 ± 2.3

[a] Electric discharge. Morton et al.[37] [b] Photolysis. Mauersberger et al.[21,45] [c] Photolysis at 293 K. Wessel Larsen et al.[40,41] [d] Photolysis. Anderson et al.[20] [e] Pulsed electron radiolysis. Sehested et al.[46] [f] This value depends on the rate constant ratio $Q + O_2 \rightarrow O + OQ/O + Q_2 \rightarrow Q + OQ$ (see text).

a slope of 1.19−1.37 passing through the origin. The exceptions to this are presented by the data for the highly enriched oxygen. Neither the mass-dependent theory of isotope effects nor the symmetry considerations discussed above would lead to the observed difference between the effects obtained using highly enriched and natural abundance oxygen.

Yang and Epstein also invoke symmetry arguments to explain the isotope effects observed in their experiments. As did Heidenreich and Thiemens,[24] they describe the symmetry effect in terms of inverse predissociation, i.e., a difference in the lifetimes of the nascent ozone due to a greater density of states for the asymmetric isotopomers. The discussion of symmetry numbers by Bates[32] makes this explanation untenable.

Morton et al.[37] also used highly enriched oxygen in their similar experiments. The ozone formed was analyzed mass spectrometrically directly, rather than being converted to oxygen before analysis, and the isotopic enrichment is reported in terms of the "enhancement" defined as

$$\text{enhancement}(\%) = 100[(^{m}O_3/^{48}O_3)_{\text{measured}}/(^{m}O_3/^{48}O_3)_{\text{statistical}} - 1] \quad (35)$$

The authors do not discuss the method they used to define the isotopic abundance ratio based only on statistics. This problem has been discussed by Margrave and Polansky.[38] For example, the relative probability of $^{50}O_3/^{48}O_3$ is given by the ratio (16−16−18 or 16−18−16)/16−16−16, which is $3(^{18}O/^{16}O)$. While the mass alone is not enough to distinguish among isotopomers, the statistical factors show that the expected abundance of some forms is small enough to be ignored. In this way, the results shown in Table 2 were obtained. These values are very high, typically larger by an order of magnitude and in the opposite direction of the values obtained by Yang and Epstein.[35,36] Perhaps some additional factor is introduced by the different methods of mass spectrometry in the two cases, i.e., direct analysis of ozone compared with analysis of oxygen produced by complete ozone decomposition. There is also the possibility that some ozone decomposed in the entrance to the mass spectrometer.

Anderson et al.[39] repeated the experiments described in the preceding paper, with the addition of using tunable infrared diode laser absorption spectroscopy to distinguish between the symmetrical and asymmetrical ozone isotopomers $^{16}O^{18}O^{16}$ and $^{18}O^{16}O^{16}O$. The oxygen used in this experiment was prepared by isotopically scrambling a mixture of ∼3% $^{18}O_2$ in natural oxygen. As in the preceding paper, the results are reported in terms of enhancement relative to a statistical distribution, with a range of values (5−16%) that includes the value reported in the preceding paper. The relative enhancement of the two possible forms of mass 50 ozone is defined by the ratio

$$R = ([^{16}O^{16}O^{18}O]/[^{16}O^{18}O^{16}O])_{\text{obs}} - 2 \quad (36)$$

The second term results from the ratio of symmetry numbers of the two isotopomers. R has values of 0.12−0.33, leading the authors to state that on a per molecule basis, the asymmetrical form carries twice the differential enhancement of the symmetrical form. There is a reasonable overlap between the results obtained in these experiments and those of Wessel Larsen et al.[40,41] described in the next section.

The value of R predicted for a mass-dependent isotope effect, i.e., the equilibrium constant ratio for the two isotopomers, can be calculated from the vibrational frequencies discussed in the Appendix, together with eq 2. The value obtained in this way is

$$R_{50} = 2.04 \exp(-19.4/T) - 2 = -0.09 \text{ at } 298 \text{ K} \quad (37)$$

in the opposite direction from the experimental result except at very high temperatures. A similar value can also be obtained from the equilibrium constants calculated by Kaye and Strobel[42] for the exchange between oxygen and the two isotopomers of ozone-^{18}O.

B. Ozone Formation in the Photolysis or Radiolysis of Oxygen-Atom Sources

In experiments carried out by Thiemens and Jackson,[43] ozone was produced by the photolysis of molecular oxygen at 157−200 nm and its isotopic composition determined. At the lower limit of this spectral region, molecular oxygen dissociates to both ^3P and ^1D atoms and ozone also dissociates. The extent of reaction in these experiments did not exceed about 1%, in which case the rate constant ratio is given by

$$(k_2/k_1) - 1 = 10^{-3}(\delta_{xf}) \tag{38}$$

The observed δ values increase rapidly with increasing pressure, reaching a relatively constant value over the range 10−140 Torr (Figure 2). For both ^{17}O and ^{18}O, these values lead to rate constant ratios of ~1.09, considerably larger than the ratios obtained in the electric discharge experiments at comparable pressures and the same temperature.[9,24] The authors suggest that the pressure dependence indicates a combination of a mass-independent effect with a mass-dependent effect, such as diffusion to the walls of the reaction vessel.

In later experiments,[44] ozone was again produced by the photolysis (155−200 or 120−160 nm) of oxygen, and the effect of oxygen pressure (2−760 Torr) on the isotopic fractionation was observed. There is no apparent difference in the results obtained with the two light sources. Contrary to earlier results[43] there is not a large decrease in δ at pressures below 10 Torr. Experiments were also performed in which air rather than pure oxygen was used as the photolysis substrate. At pressures between about 200 and 760 Torr and a temperature of 295 K, $^{18}\delta$ is fairly constant at a value of 90−100‰, in agreement with the results of the preceding paper. Lower pressures increase this value to as much as 140‰, in contrast to the pressure effect noted previously. The relative isotope effect ratio $^{17}\delta/^{18}\delta$ ranges from 0.80 to 0.95. These experiments were carried out using a larger reaction vessel than that used in the previous work, and the authors suggest that the slower diffusion of ozone to the cold walls may have led to photolysis of the ozone product, which is known to have a mass-dependent isotope effect.

Further experiments carried out by Thiemens and Jackson[28] determined the effect of still higher pressures (up to 87 atm) when ozone was produced by the photolysis of oxygen at ~184 nm. The significant observation is that $^{17}\delta$ and $^{18}\delta$ values both decrease from ~80‰ at 1 atm to slightly negative values (<−10‰) at pressures above about 50 atm. In the low-pressure region, a plot of $^{17}\delta$ vs $^{18}\delta$ has a slope of approximately unity, in agreement with earlier experiments from this group. At higher pressures, the slope seems to be ~0.5, as would be expected from a mass-dependent isotope effect, but the few points obtained in this pressure region make such an observation tenuous at best.

Morton et al.[22] report on experiments in which mixtures of 0.1 Torr of ozone and various pressures of oxygen (5−1000 Torr) were exposed to visible light, which was filtered to isolate 590 nm, within the Chappuis band (440−850 nm). At this wavelength, oxygen does not absorb light and no electronically excited oxygen atoms or molecules can be produced from the photodissociation of ozone, the source of O (^3P) atoms. The procedure described is designed to ensure equilibration of the ozone and oxygen. At a temperature of ~320 K, the enhancement of ^{18}O decreased from about 13% to about 8% as the pressure increased from 5 to 1000 Torr. A similar effect on $^{17}\delta$ was observed, and the average value of the ratio $^{17}\delta/^{18}\delta$ was 0.9. The magnitude of the enhancement in the ozone is comparable to that measured by Thiemens and Jackson.[44] The temperature effect on the enhancement was determined over the range 150−400 K, and the enhancement increases from a few percent at the lower end of the temperature range to 10−15% at the upper end, similar to the temperature effect found in the electric discharge experiments.

The equilibrium isotopic fractionation expected on the basis of a mass-dependent isotope effect can be calculated from the relevant equilibrium constants for isotope exchange:

$$OQ + O_3 \rightleftarrows O_2 + QOO,\ K_a \tag{39}$$

$$OQ + O_3 \rightleftarrows O_2 + OQO,\ K_s \tag{40}$$

These equilibrium constants have been calculated by Kaye and Strobel,[42] with the resulting values of 0.974 and 0.508 for K_a and K_s, respectively, at 298 K. A calculation using the more recently obtained vibrational frequencies discussed in the Appendix leads to values of 0.976 and 0.509 at 298.1 K, in excellent agreement with the earlier calculations. Thus, the predicted ratio R_{ozone}/R_{oxygen} is given by

$$\frac{[QOO] + [OQO]}{[O_3]} / \frac{[QO]}{[O_2]} = K_a + K_s \tag{41}$$

The value of 1.48 obtained from both sets of calculations is essentially the statistical value of 3/2 resulting from symmetry numbers, predicting that no isotopic enhancement would be observed.

The experiments of Morton et al.[37] in which highly enriched oxygen was used were extended by Mauersberger et al.[45] by using photolysis instead of an electric discharge. The results were very similar to those previously obtained with an electric discharge and are shown in Table 2 and Figure 3.

Wessel Larsen et al.[40,41] used high-resolution microwave spectroscopy to distinguish between OOO, OOQ, OQO, OQQ, QOQ, and QQQ (O = ^{16}O, Q = ^{18}O; unfortunately they did not extend these experiments to include ^{17}O). Photolysis of ozone (of normal isotopic composition) in the Hartley bands (200−300 nm) or the Chappuis bands (440−850 nm) was the source of oxygen atoms, which then reacted with mixtures of O_2 and Q_2 of roughly equal concentrations. These experiments were designed to test whether the O + Q_2 reaction proceeds via end-on attack or a mechanism involving the symmetrical OQO and QOQ species. The conclusion was that end-on attack predominates. The experiments also provide additional data on isotope effects, and the results are given in Table 2. Within the rather wide error limits cited by the authors, the results are in agreement with those of Mauersberger et al.,[45] particularly as to the very small enhancement of $^{54}O_3$. The value of R was also measured by Wessel Larsen et al.,[40,41] and

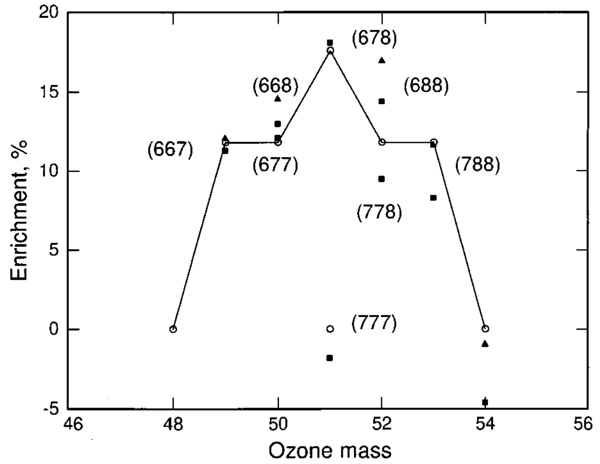


Figure 3. Isotopic enrichment of ozone produced in an electric discharge in oxygen,[37] (▲) in photolysis of oxygen,[21,45] (■). Predictions of the symmetry model described by Gellene[70] are indicated by the open circles and solid lines. The numbers in parentheses abbreviate the isotopic composition of the ozone molecule, e.g., (667) = $^{16}O^{16}O^{17}O$ and $^{16}O^{17}O^{16}O$. No enrichment is predicted for the symmetrical reactions leading to (777) or (888).

Table 3. Rate Constant Ratios for Ozone Formation[a]

ozone mass	reaction	$k(X + YZ)/k(O + OO)$		reaction	$k(X + YZ)/k(O + OO)$	
48	O + OO	(1.00)				
49	P + OO	1.03		O + OP	1.17	
50	Q + OO	0.93	1.147[b]	O + OQ	1.27	1.036[b]
50	O + PP	1.23		P + OP	1.11	
51	P + PP			P + PP	1.02	
52	O + QQ	1.53	1.147[b]	Q + OQ	1.01	1.036[b]
52	Q + PP	1.03		P + PQ	1.21	
53	P + QQ	1.31		Q + PQ	1.09	
54	Q + QQ	1.03	1.098			
reference		21[c]	46[d]		21[e]	46

[a] O = ^{16}O; P = ^{17}O; Q = ^{18}O. [b] Only the average value of the two rate constant ratios is obtained. [c] Photolysis, from measured rate constants. [d] Radiolysis. [e] Photolysis, from derived rate constants.

the ratios for both $^{50}O_3$ and $^{52}O_3$ ($^{16}O^{18}O^{18}O$ and $^{18}O^{16}O^{18}O$) were obtained at various pressures of nitrogen, added as an inert gas. In both cases, the values of R increased with increasing pressure: R_{50} ranges from 0.10 to 0.35 and R_{52} varies from −0.03 to 0.27. However, the most interesting point raised by these experiments results from calculations modeling the reaction kinetics of forming the various isotopologues of ozone, as well as the scrambling reactions $O + Q_2 \rightarrow OQ + Q$ and $Q + O_2 \rightarrow OQ + O$. The rate constants[19] for these exchange reactions are 1 or 2 orders of magnitude (depending on temperature) larger than those for the ozone formation reactions, and they lead to an equality of the isotopic composition in atomic and molecular oxygen. However, because in these experiments the concentration of atoms is very low, the scrambling reaction does not reach steady state before ozone formation takes place to a considerable extent. The result is that even when the rate constants for formation of various isotopologues of ozone are assumed to be equal (i.e., *no kinetic isotope effect*), the ratios R_{50} and R_{52} (see above) are not predicted to reach the equilibrium value of 2 until substantial amounts of ozone have been produced. In fact, to obtain qualitative agreement between the simulations and experiments at 143 K, the authors had to increase the rate constant for the scrambling reaction by a factor of about 5 times the reported value. I confirmed these calculations, which emphasize the fact that the expected isotopic enrichment depends on the extent to which reaction has occurred, a parameter that has not been consistently reported in experiments designed to probe mass-independent isotope effects.

Sehested et al.[46] recently carried out experiments which, in my opinion, are the cleanest and most definitive studies of the kinetic isotope effect in the ozone-forming reaction, unfortunately using only ^{18}O and ^{16}O. The simplicity of these experiments derives from the fact that the reactant oxygen atoms are formed by the pulsed radiolysis of carbon dioxide in various mixtures of $^{16}O_2$, $^{18}O_2$, and $^{16}O^{18}O$, and unlike the experiments involving mixtures of ozone and oxygen, there is no rapid isotopic exchange between ozone and the oxygen-atom source. The 10-fold excess of $C^{16}O_2$ ensures that essentially all the oxygen atoms are derived from this source and not from the molecular oxygen. Experiments showed that the isotopic composition of carbon dioxide did not change during the course of the photolysis. The total rate of formation of ozone was measured using UV absorption spectrometry at 254 nm. First-order rate constants for reactions O + OO and Q + QQ were obtained directly, leading to the ratio given in Table 3. Note that the rate constants are not equal, even though the symmetries of reactants and transition states must be the same for both systems. An average of the rate constants for Q + OO and O + QQ was obtained from experiments with equimolar mixtures of O_2 and Q_2. For the reactions Q or O + OQ, an equilibrated mixture of O_2, Q_2, and OQ was used. The ratios are shown in Table 3. A discussion of mass-dependent isotope effects calculated for these reactions is given in the Appendix.

Experiments in which similar mixtures of oxygen isotopologues serving as the source of both atomic and molecular reactants were recently reported by Anderson et al.[20] and Mauersberger et al.[21] The results obtained in the second series of experiments will be discussed. Photolysis at 180 nm was the source of atoms, and the concentration of ozone product molecules was determined mass spectrometrically. The extent of reaction was kept low in order to reduce isotopic scrambling among the molecular oxygen. The rate constants for a number of isotopic combinations relative to the rate constant for $^{16}O + {}^{16}O^{16}O$ are given in Table 3. The most interesting feature of the results obtained in this work is the observation that rate constants for O + O_2, Q + O_2, and Q + Q_2 are nearly equal while the rate constant for O + Q_2 is about 50% larger (Table 3). The radiolysis experiments of Sehested et al.[46] do not provide a rate constant for this reaction, but they do indicate that Q + Q_2 is about 10% faster than O + O_2, in disagreement with these results. It might be noted that the experiments of Sehested et al., Anderson et al., and Mauersberger et al. are carried out in the termolecular pressure regime. The radiolysis experiments were carried out with a bath gas of about

1 atm of carbon dioxide, while the photolysis experiments were at 200 Torr of nitrogen as the bath gas. It seems unlikely that this can have an effect on the *relative* rate constants. The rate constant ratios shown in Table 3 are for reactions of various symmetries, and there seems to be no consistent pattern that can be ascribed to a symmetry effect.

C. Thermal and Photolytic Decomposition of Ozone to Oxygen

Valentini et al.[47] used CARS (coherent anti-Stokes Raman spectroscopy) to examine the $O_2(^1\Delta_g)$ produced in the photolysis of ozone at wavelengths between 230 and 311 nm. At these wavelengths excitation to a single excited state leads to two product channels due to curve crossing in the photolysis exit channel:

$$O_3 + h\nu \rightarrow O_2(^1\Delta_g) + O(^1D) \qquad (42)$$

$$\rightarrow O_2(^3\Sigma_g) + O(^3P) \qquad (43)$$

They observed that in the photodissociation of $^{48}O_3$ the rotational population in the even J levels of the $O_2(^1\Delta_g)$ product is greater than that in the odd J levels. Using ozone enriched in ^{18}O, they showed that this is not the case for $^{18}O^{16}O$ and by inference for $^{17}O^{16}O$. In a second paper discussing the photolysis of ozone and related questions, Valentini[48] expands his explanation of the ^{17}O and ^{18}O depletion in the $O_2(^1\Delta_g)$ product. The aforementioned crossing of the potential-energy curves for the $O_2(^1\Delta_g) + O(^1D)$ and $O_2(^3\Sigma_g) + O(^3P)$ states provides a mechanism for the formation of $O_2(^3\Sigma_g)$ from the initially excited state of ozone formed by absorption of a UV photon. The selection rule for this crossing is $\Delta J = 0, \pm2, \pm4, ...$ When this is coupled with the fact that a homonuclear diatomic with no nuclear spins has only odd-J states in the ground electronic state, it introduces the requirement that only odd-J states of O_2 $(^1\Delta)$ will undergo curve crossing, and this population will be depleted. This symmetry restriction does not apply to heteronuclear molecules, and hence, both even-J and odd-J states of ozone containing ^{17}O or ^{18}O can undergo curve crossing to $^{17}O^{16}O$ or $^{18}O^{16}O$ in the ground electronic state. This introduces a mass-independent fractionation in the photolysis, increasing the heavy isotope abundance in the product oxygen.

The application of this explanation to the formation of ozone by an electric discharge in oxygen is based on the fact that a substantial fraction (~0.1) of the oxygen is in the $^1\Delta_g$ state. The same restrictions that applied in the photolysis will apply to the nonadiabatic collisional relaxation to the $^3\Sigma_g$ state, leading to mass-independent enrichment of the heavy isotopes. Only oxygen in the triplet ground state can enter the recombination process

$$OQ(^3\Sigma_g) + O(^3P) + O_2 \rightarrow OQO \text{ or } OOQ + O_2 \qquad (44)$$

Valentini concludes that the ozone thus formed will be enriched in either heavy isotope by about 50‰, which is comparable to the enrichment observed by Heidenreich and Thiemens[23] at high pressures. A number of competing reactions can occur, the most important of which is the resonant energy transfer

$$OQ(^1\Delta_g) + OO(^3\Sigma_g) \rightarrow OO(^1\Delta_g) + OQ(^3\Sigma_g) \qquad (45)$$

which competes with the ozone-forming recombination. Also, at low pressures, the termolecular formation of ozone will lose out to atom exchange processes of the type

$$O(^3P) + OQ(^1\Delta_g) \rightarrow Q(^3P) + OO(^1\Delta_g) \qquad (46)$$

which will lead to isotopic scrambling. The observed mass-dependent *depletions* in the heavy isotopes at low pressures are approximately equal to those calculated by Kaye[23] for the recombination reaction.

A point which Valentini did not make is that an OOQ molecule can be formed either from a heavy OQ molecule (enhanced) + a light O atom or from a light OO molecule (depleted) + a heavy Q atom. This will decrease the expected symmetry effect. Valentini's papers appeared before the work of Morton et al.,[37] in which ozone of masses 48−54 was produced. How does the Valentini theory fit this data? This symmetry-based explanation of mass-independent isotope effects would not predict a difference between $^{18}O_2$ and $^{16}O_2$, since both of these molecules are allowed only odd J rotational levels. The observation of a small negative enhancement of −9‰ for mass 54 would fit the theory. However, as Table 2 indicates, the experimental data[20,46] are not in agreement with each other, even as to the sign of the isotope effect. In addition, the effect on $^{50}O_3$ formed from $^{18}O^{16}O$ + ^{16}O should be the same as that for $^{52}O_3$ formed from $^{18}O^{16}O$ + ^{18}O, which is approximately correct. Also, the greatest enhancement was observed for the completely unsymmetric molecule $^{16}O^{17}O^{18}O$. This can only be formed from a heteronuclear molecule, unlike the case for the QOO molecules, so again the Valentini theory fits, at least qualitatively. Because reaction 45 is bimolecular and reaction 44 is termolecular, the isotopic enrichment would be predicted to increase with increasing pressure, as observed in earlier experiments.[24,43] However, later experiments carried out at much higher pressures[28] show the opposite pressure dependence.

Bhattacharya and Thiemens[49] studied the photolytic and thermal decomposition of ozone, and the oxygen product was analyzed mass spectrometrically. Both solid and gaseous ozone were subjected to 180−260 nm photolysis. Thermal decomposition was carried out at 25 °C and with added helium at 50−60 °C. Qualitatively it appears that the oxygen product is depleted in the heavy isotopes, both in the photolysis and the thermal decomposition. The authors define the relative ^{17}O and ^{18}O effects by

$$\text{slope} = [^{17}\delta(O_3) - {}^{17}\delta(O_2)]/[^{18}\delta(O_3) - {}^{18}\delta(O_2)] \qquad (47)$$

and find an average value of 0.59, not very different from the value calculated by Kaye.[23] The symmetry considerations proposed by Valentini[48] should also be applicable to the photolysis of ozone studied by Bhattacharya and Thiemens[49] and Wen and

Thiemens,[50] but on the contrary, the heavy isotopes were found to be *depleted* in the oxygen product.

Wen and Thiemens[50,51] studied the thermal dissociation of ozone at various temperatures, and the isotopic compositions of the product oxygen and the remaining ozone were determined. From the oxygen data, the ratio k_{18}/k_{16} ranges from 0.98 at 20 °C to 1.03 at the highest temperature, 120 °C. A "physical chemist's plot" of $\ln(k_{18}/k_{16})$ against the reciprocal of the temperature leads to a straight line with little scatter in the data if the three points at the lowest temperatures are excluded. This line leads to a ratio of preexponential factors (A_{18}/A_{16}) of 1.28, in the opposite direction from what one would expect for a bond-breaking reaction; it is abnormally large for a mass-dependent effect. The activation energy difference, $\Delta E_{act} = -85$ K, is in the direction such that the activation energy is larger for the heavier isotope.

In a later paper, Wen and Thiemens[50] describe in more detail the thermal gas-phase decomposition of ozone at 90 and 110 °C. In addition, the room-temperature photolysis using 532 and 254 nm light was studied. The data are sufficiently detailed to permit calculations of rate constant ratios using eqs 19−23. At 90 °C, both the residual ozone and product oxygen data lead to the same values of k_{18}/k_{16}, which range from 1.005 to 1.020 with an average of about 1.013. As the $^{17}\delta$ and $^{18}\delta$ values are nearly equal in all these experiments, a similar result will be obtained for k_{17}/k_{16}. At 110 °C, the scatter is somewhat less and the average k_{18}/k_{16} ratio is 1.023. These values are in good agreement with the values one would calculate from the preexponential factor and activation energy difference discussed in the preceding paragraph. In these thermal experiments, the oxygen product is enriched in the heavy isotopes, whereas the opposite effect is observed in the photolysis experiments.[49,50]

The mechanism for the thermal decomposition of ozone is well established:

$$O_3 + M \rightarrow O_2 + O + M, \quad k_1 \tag{48}$$

$$O + O_2 + M \rightarrow O_3, \; k_{-1} \tag{49}$$

$$O + O_3 \rightarrow 2O_2, \; k_2 \tag{50}$$

The rate expression for the disappearance of ozone is

$$-d[O_3]/dt = 2k_1k_2[O_3]^2[M]/(k_{-1}[O_2][M] + k_2[O_3]) \tag{51}$$

Under the conditions used by Wen and Thiemens, $k_{-1}[O_2][M]$ is negligible with respect to the second term in the denominator (Zaslowsky et al.[52]) and the rate expression simplifies to

$$-d[O_3]/dt = 2k_1[O_3][M] \tag{52}$$

Thus, the measured kinetic isotope effect should simply be that for the unimolecular decomposition of ozone. The calculations by Kaye[23] using the conventional mass-dependent approach provide these ratios:

$$^{17}\delta = [k(^{17}O^{16}O^{16}O)/k(^{16}O^{16}O^{16}O)] - 1 = -6‰ \tag{53}$$

$$^{17}\delta = [k(^{16}O^{17}O^{16}O)/k(^{16}O^{16}O^{16}O)] - 1 = -3‰$$

The δ values for the ^{18}O reactions are approximately twice this large. These are in the opposite direction from the experimental values, which indicate that the heavy isotopologue reacts more rapidly.

The ozone decomposition was also modeled by Wen and Thiemens[50] with a complex reaction mechanism consisting of about 30 elementary reactions, some of which are isotopic variants of reactions 48−50. They then arbitrarily varied the rate constants k_1 and k_{-1} for the ^{17}O and ^{18}O variations of the above reactions in order to fit the observed isotopic composition of the remaining ozone as a function of the extent of decomposition. The best fits were found with the following rate constant ratios: $k_1(^{17}O)/k_1(^{16}O) = k_1(^{18}O)/k_1(^{16}O) = 1.05$ and $k_{-1}(^{17}O)/k_{-1}(^{16}O) = k_{-1}(^{18}O)/k_{-1}(^{16}O) = 1.10$ for the thermal reaction at 383 K. The model calculations assumed no isotope effect on k_2. In the photolysis experiments at 532 nm, the same ratio was found for the k_{-1} rate constants but the ratios for k_1 were 0.972 for ^{18}O and 0.988 for ^{17}O. Note that the isotope effect has changed direction in this case.

These thermal decomposition experiments are important as a sort of ground zero for the mass-independent isotope effect. The reaction should not involve excited atoms or molecules, unlike electric discharge or photochemical reactions. The mechanism of the reaction is well understood and relatively simple. On the other hand, ozone presents experimental difficulties because of its instability—it is subject to catalytic decomposition caused by surface reactions or the presence of trace amounts of nitrogen oxides. The observation in thermal reactions of isotope effects that do not fit into the framework of conventional mass-dependent theory is an important piece of evidence supporting the existence of mass-independent effects.

D. Formation and Dissociation of Carbon Dioxide

As indicated in the preceding section, ozone is a somewhat difficult substance to work with because of its instability. Thus, it is significant that reactions involving other molecules have also provided evidence for mass-independent isotope effects.

Soon after the initial report of such effects, Heidenreich and Thiemens[26] used an electric discharge to dissociate carbon dioxide, with subsequent isotopic analysis of the mixture of carbon dioxide and oxygen. The extent of reaction is small enough so that the relation between the initial isotopic composition of the carbon dioxide and the isotopic composition of the product oxygen is given by eq 38. This leads to an average value of 0.973 for the rate constant ratio k_{18}/k_{16}, not an unreasonable kinetic isotope effect. However, the mass-independent effect is demonstrated by the ratio $^{17}\delta/^{18}\delta = 0.7$. The mechanism for the process taking place in the electric discharge is not well established but must involve the formation of oxygen atoms that can exchange with carbon dioxide. The oxygen exchange reaction has been observed previously in the quenching of O(^{1}D) by CO_2 and is believed to take place through the formation of a CO_3 intermediate with three equivalent C−O bonds.[53,54]

To test the assumed O-atom exchange mechanism, Wen and Thiemens[55] used ozone photolysis as a source of excited oxygen atoms:

$$O_3 + h\nu\ (\lambda < 310\ \text{nm}) \rightarrow O_2(^1\Delta) + O(^1D) \quad (54)$$

Ozone of known amount and isotopic composition was prepared by an electric discharge. It was then mixed with carbon dioxide of known isotopic composition, and O(^{1}D) atoms were formed by photolysis at various wavelengths. In addition to the proposed exchange of oxygen atoms with carbon dioxide, O atoms and excited oxygen molecules react with ozone:

$$^{m}O(^1D) + C^{16}O_2 \rightarrow [^{m}OC^{16}O_2] \rightarrow {}^{16}O(^3P) + {}^{m}OC^{16}O \quad (55)$$

$$O(^3P) + O_3 \rightarrow 2O_2 \quad (56)$$

$$O(^1D) + O_3 \rightarrow 2O_2 \quad (57)$$

$$O_2(^1\Delta) + O_3 \rightarrow O(^3P) + 2O_2 \quad (58)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (59)$$

All the ozone was converted to oxygen during the photolysis, so that in the absence of exchange with carbon dioxide, the isotopic composition of the oxygen product should be the same as that of the initial ozone. Small increases in $^{18}\delta$ and $^{17}\delta$ of the carbon dioxide were observed in photolysis at 254 nm, presumably from the exchange of carbon dioxide with O(^{1}D). The oxygen product is depleted in both ^{17}O and ^{18}O, as is the case for 532 nm photolysis of pure ozone.[50] Combined 254 and 185 nm radiation produced larger enrichments. Presumably the shorter wavelength leads to the photolysis of the oxygen product, forming O(^{3}P) which does not exchange with carbon dioxide but can react with ozone to form molecular oxygen or recombine with oxygen molecules to form ozone in a three-body collision. Photolysis at 532 nm, producing only O(^{3}P), leads to no change in the isotopic composition of the oxygen product, again suggesting that the reaction of O(^{1}D) atoms with carbon dioxide is the mechanism of the exchange. A plot of $^{17}\delta$ against $^{18}\delta$ for the oxygen formed in the photolysis gives a straight line with a slope of about 0.75, falling between the limits expected for a completely mass-dependent and a completely mass-independent process. The authors argue that the increase in heavy isotope depletion of the O_2 product with increasing pressure results from an increase in exchange relative to electronic quenching of the O(^{1}D), but both processes should depend linearly on the carbon dioxide pressure.

In a more recent paper, Yung et al.[56] expand the above mechanism and apply it to simulate the laboratory experiments of Wen and Thiemens,[55] in which both ^{17}O and ^{18}O effects were observed. In their most successful model, they assume that the rate constant for formation of $^{50}O_3$ is larger than that for $^{48}O_3$ by 9%. This is in the opposite direction from the ratio determined by Anderson et al.[17] for the Q + O_2 reaction and smaller than the ratio determined for the O + OQ reaction. Using the isotopic composition of reactants quoted by Wen and Thiemens, the authors find $^{18}\delta$ values for ozone that cluster around −75‰, in good agreement with the experimental results. However, if the isotope effect on rate constants was assumed the same for ^{17}O as for ^{18}O in the calculations, the $^{17}\delta$ values were about −78‰, compared to experimental values clustered about −55‰. A better fit is obtained if the $^{17}O + {}^{32}O_2$ and $^{16}O + {}^{16}O^{17}O$ and isotope effects are assume to be two-thirds as large as the isotope effects for $^{18}O + {}^{32}O_2$ and $^{16}O + {}^{16}O^{18}O$ reactions, which is closer to the mass-dependent effect. Yung et al. combine their reaction mechanism and rate constants with an atmospheric model to calculate oxygen isotopic abundances in atmospheric carbon dioxide as a function of altitude. This is discussed in section IVD.

As the above reactions indicate, this is a very complicated system, making it difficult or impossible to isolate individual processes that may be contributing to the observed isotope effects. The rate constants for the quenching of O(^{1}D) by carbon dioxide and ozone are essentially the same, and quenching by carbon dioxide leads to exchange in nearly every collision. Hence, the product oxygen will represent isotopic scrambling between oxygen, ozone, and carbon dioxide. Rate constants for the other reactions are a few orders of magnitude smaller. Wen and Thiemens[55] believe that a photochemical steady state is established between molecular oxygen and carbon dioxide. Calculated equilibrium constants for this isotope exchange process

$$^{18}O^{16}O + {}^{16}OC^{16}O \rightleftarrows {}^{16}O_2 + {}^{18}OC^{16}O \quad (60)$$

are given by Urey.[3] At 298.1 K, this equilibrium constant is 1.033, indicating a depletion of the heavy isotopes in molecular oxygen and an enrichment in carbon dioxide, in agreement with the experiment. The question of symmetry effects in the formation of carbon dioxide from oxygen atoms and carbon monoxide was discussed in a later paper by Bates[57] in which he again demonstrated that the proper calculation of symmetry numbers did not lead to an enhancement of the unsymmetrical molecule.

E. Reactions Involving Carbon Monoxide

A somewhat different approach was used by Bhattacharya and Thiemens[58] in experiments in which oxygen atoms reacted with carbon monoxide to form carbon dioxide. The oxygen atoms were formed by the photodissociation of O_2 by a mercury lamp (180−260 nm) or a krypton lamp (120−160 nm). The threshold for O(^{1}D) formation in the photodissociation of O_2 is 175 nm, so irradiation with a Hg lamp should produce only ground-state O(^{3}P) atoms. To minimize ozone formation, a large excess of CO was used. The carbon dioxide formed contains both ^{13}C and ^{17}O, and to avoid problems of mass spectrometric analysis, it was converted to O_2 and CF_4 using BrF_5. Values of $^{17}\delta$ and $^{18}\delta$ as large as ~60 ‰ were observed, and a linear relation between the two with $^{17}\delta = 0.82(^{18}\delta)$ was found. No correlation of δ values with the extent of reaction, initial CO/O_2 ratio, or photolysis time is evident. Blank experiments showed that in the absence of oxygen, no carbon dioxide was formed. In addition, there is considerable evidence that ozone is not involved in the reaction. In the experiments using the Kr lamp, there is a possible contribution from photolysis of the carbon dioxide that has been formed. Although the $^{17}\delta/^{18}\delta$ ratio from the Kr lamp photolysis is about the same as that obtained with the Hg lamp, each δ value appears larger in the Kr photolysis. The authors believe that the observed isotopic fractionation is the result of a combined exchange of oxygen atoms with CO, followed by the mass-independent recombination of O and CO. At 300 K and the pressures of these experiments, the rates for these two processes are approximately equal.

Attempting to account for the observed mass-independent oxygen isotopic distribution in atmospheric carbon monoxide, Röckmann et al.[12,59] investigated various reactions in which this compound is a reactant or product. In particular, they searched for a reaction in which the observed isotopic distribution in atmospheric ozone (see below) could be transferred to CO. As many natural non-methane hydrocarbons are oxidized by ozone rather than by OH, this is a potential source of such an effect. The hydrocarbons investigated were ethene (C_2H_4), isoprene (C_5H_8), and β-pinene ($C_{10}H_{16}$).[59] Ozone was generated by the photolysis of oxygen with a low-pressure mercury lamp, and its isotopic composition was determined mass spectrometrically. The observed $^{17}\delta$ and $^{18}\delta$ values were similar to those measured for this reaction by Thiemens and Jackson[43] and again $^{17}\delta \simeq {}^{18}\delta$. In the reaction experiments, the hydrocarbon was added to the mixture of ozone and oxygen and the course of reaction was followed with FTIR absorption spectroscopy. After removal of the unreacted ozone, the remaining CO was subjected to mass spectrometric analysis. A fairly wide range of isotopic enrichment relative to the oxygen used for ozone production was observed, from $^{18}\delta = 46‰$ for isoprene with water added to 82‰ for ethene (slightly greater than that for the ozone reactant). In all cases, the values of $^{17}\delta$ and $^{18}\delta$ were nearly equal. The implications of these isotope effects for the atmospheric budget of CO are discussed below.

The reaction $OH + CO \rightarrow H + CO_2$ is the main atmospheric path for removal of carbon monoxide, and it is also important in combustion chemistry. Kinetic isotope effects of ^{13}C and ^{18}O were studied a number of years ago by Stevens et al.,[60] but there was no comparison of ^{18}O and ^{17}O. Such a comparison was made recently by Röckmann et al.,[12] who also repeated the earlier determinations of the carbon isotope effect. A mixture of He, CO, and hydrogen peroxide was circulated through a photochemical reactor in which OH was produced by photolysis of the H_2O_2 by a Xe lamp ($\lambda > 190$ nm). Ratios of rate constants were obtained from the isotopic composition of the unreacted CO, using eq 21. In determining the $^{17}O/^{16}O$ ratio, the unreacted CO was first converted to O_2 in order to avoid interference by $^{13}C^{16}O/^{12}C^{16}O$; this was not necessary for the $^{18}O/^{16}O$ ratio. With the definition $\epsilon^{m}O$ (‰) $= 10^3[(^{16}k/^{m}k) - 1]$, values of $\epsilon^{18}O$ of ca. -10 were found; i.e., this is an inverse effect in which the heavier isotope reacts more rapidly. The ^{13}C and ^{18}O results are in good agreement with those from the earlier experiments of Stevens et al.[60] The value is relatively insensitive to total pressure in a bath gas of nitrogen or mixtures of nitrogen and oxygen but is almost twice as negative in helium. A similar presssure dependence was observed in the earlier work.[60] The effect of ^{17}O is reported in terms of the quantity $E^{17}O$ (‰) $\equiv \epsilon^{17}O - 0.52(\epsilon^{18}O)$, and this does show a slight pressure dependence, increasing from ~2.5‰ to 4.5‰ as the bath gas pressure increases from 250 to 880 mbar. The values are smaller for He as a bath gas. Although the authors describe these results as evidence for mass-independent isotope fractionation, they do not fit into the array of other mass-independent effects that have been observed, in which $\epsilon^{17}O \simeq \epsilon^{18}O$. In fact, if this equality is exact, then $E^{17}O = 0.48(\epsilon^{18}O)$. On the other hand, if a mass-dependent isotope effect prevails, then $E^{17}O$ is zero, by definition. As Figure 4 shows, the observed values of $E^{17}O$ do not lie between these two limits, a result of the fact that $\epsilon^{17}O$ is even *smaller* than would be predicted by a normal mass-dependent effect. This reaction should provide a good test for the existence of mass-independent isotope effects, and it is to be hoped that it will be studied further. The significance of the isotopic fractionation of carbon monoxide to the atmospheric chemistry of this compound is discussed below.

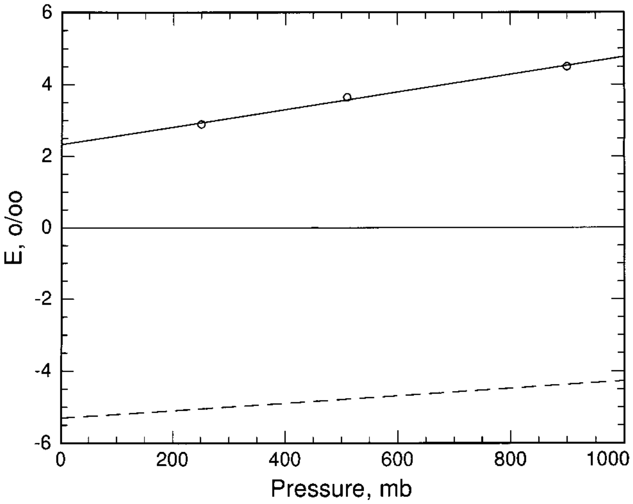


Figure 4. Oxygen isotope effect in the reaction $CO + OH \rightarrow CO_2 + H$ as a function of total pressure. In this plot, measured values[12] of $E \equiv [(^{16}k/^{17}k) - 1] - 0.52[(^{16}k/^{18}k) - 1]$ (○) are compared with the values predicted for a normal mass-dependent isotope effect (—) and predicted for equal ^{17}O and ^{18}O isotope effects (- - -).

F. Reactions Involving Sulfur Isotopes

In a search for mass-independent isotope effects involving elements other than oxygen, Bains-Sahota and Thiemens[61] investigated the formation of S_2F_{10} by an electric discharge in sulfur tetrafluoride. To establish a value for a mass-dependent process involving the three sulfur isotopes ^{32}S, ^{33}S, and ^{34}S, the authors allowed sulfur hexafluoride to flow through a molecular sieve trap. The values of $^{33}\delta$ plotted against $^{34}\delta$ from this experiment lie on a straight line with a slope of 0.505. In gaseous diffusion, the isotope effect depends on the square root of the *molecular* masses, which would lead to a ratio of 0.501, in excellent agreement with the experiments. Similar plots of the enrichment values for the ^{33}S and ^{34}S isotopes in the reaction products lead to slopes of 0.541 (their Table I) and 0.526 (their Table II). These values can be compared with the mass-dependent value obtained from the prediction of eq 11, which leads to a ratio of 0.515. In any case, the small difference between the observed values and the mass-dependent value leads the authors to assume that the observed fractionation is the result of a combined mass-dependent effect (about 90% of the total) and a small contribution from a mass-independent effect. However, the small differences from the predicted mass-dependent effect (a few percent) could also be the result of the approximations inherent in eq 9. Bains-Sahota and Thiemens believe that the mass-independent effect results from the formation of the S_2F_{10} molecule by recombination of two SF_5 radicals. Electrons from the electric discharge subsequently dissociate the S_2F_{10} to SF_4 and SF_6.

More recently, Colman et al.[62] reported measurements of sulfur isotope abundances in samples of the polymer formed in the UV and solar photolysis of carbon disulfide. The solid polymeric material formed in the solar photolysis had an anomalous isotopic composition; it was mass-independently enriched in ^{33}S and depleted in ^{36}S (by as much as 90‰) relative to ^{34}S. The implications for meteorites and the atmosphere of Jupiter are discussed in this paper.

A very recent report by Lee and Thiemens[63] discusses the distribution of sulfur isotopes in atmospheric sulfate aerosols. Small particle sulfate aerosols were found to be more enriched in ^{18}O than were large particles. The isotopes were reported to be mass-independently fractionated.

G. Ion–Molecule Reactions

Gellene and co-workers found remarkably large and mass-independent isotope effects in ion–molecule reactions of the type $A^+ + A \rightarrow A_2^+$. The first of these studies[64] was of the formation of O_4^+, which takes place according to the mechanism

$$O_2 + e^- \rightarrow O_2^+ + 2\,e^- \tag{61}$$

$$O_2^+ + 2O_2 \rightarrow O_4^+ + O_2 \tag{62}$$

Experiments were also carried out with oxygen–rare-gas mixtures. The results are expressed in terms of the isotopic ratio of ion intensities. All experiments were carried out with oxygen containing a natural abundance of isotopes. At the lowest electron energy used (~16 eV), the enrichment is about a factor of 10 for both isotopes, corresponding to an astonishing value of $\delta = 9000$‰. Although the ^{17}O and ^{18}O effects are not equal in this particular reaction, the magnitude is large enough to indicate that something other than a mass-dependent effect is involved. Because the extent of reaction is not indicated in this paper (or the others describing ion–molecule cluster formation), it is impossible to determine the rate constant ratio from the data reported.

A somewhat simpler case is presented by the analogous reaction in helium,[65] which was investigated by adding ^3He (10% or 50%) to natural abundance helium and measuring the mass 7/mass 8 ratio or the mass 7/mass 6 ratio corresponding to the dimer ion He_2^+. With the 10% ^3He sample, the mass 7/mass 8 ratio was about 2.5 times the statistical value at the lowest inlet pressure but decreased to unity at pressures above ~150 mTorr. A similar maximum effect for mass 7/mass 6 was observed for the 50% ^3He sample, but the decrease with inlet pressure was more rapid. Gellene discusses the probable magnitude of mass-dependent rate constants involved in this reaction and concludes that it is much smaller than the observed effect. It is also significant that the concentration of the $^3He-^4He^+$ cluster is enhanced with respect to that of both the $^3He-^3He$ and $^4He-^4He$ clusters. Gellene ascribes this to a symmetry-induced kinetic isotope effect (SIKIE), which is discussed later in this section.

Further evidence for an SIKIE was provided by the $CO_2^+ + CO_2 \rightarrow (CO_2)_2^+$ reaction, in which both ^{13}C and ^{18}O effects could be observed.[66] The masses of the dimer ion substituted with ^{17}O and ^{13}C are the same, but a correction for ^{17}O can be made with the assumption that ^{17}O and ^{18}O effects are equal. The result is that the $^{18}O/^{16}O$ enhancement reaches a maximum of about a factor of 20, decreasing rapidly with increasing pressure and also with increasing electron energy. The $^{13}C/^{12}C$ effect has a maximum of about 5, again drops rapidly with pressure, but is almost independent of electron energy. The decrease with pressure is attributed to isotope scrambling in the dimer ion, which ultimately leads to equilibrium. Symmetry arguments indicate that the $^{13}C/^{12}C$ effect on the ion–molecule combination reaction should be 2 at most, indicating that a SIKIE in the dissociation or stabilization of the complex may also be present. The effect of ^{17}O or ^{18}O substitution destroys the symmetry of the carbon dioxide molecule or ion and leads to a different type of SIKIE, which according to Gellene's analysis is applicable only to the ion. This results from the differing propensities for ionization by electrons to produce ions with *e* or *f* parity labeling.

This latter consideration implies that the replacement of CO_2 (but not the ion) by another closed-shell species would still lead to a SIKIE. This was tested by examining the reaction of Ar with CO_2^+.[67] The ^{18}O enhancement reaches a low-pressure maximum of about 20, decreasing with increasing pressure and with an increase in the Ar/CO_2 ratio.

Gellene and co-workers developed a symmetry-based theory of mass-independent isotope effects to explain their observations of ion–molecule cluster yields. Correlation rules for molecular reactions are usually based on the symmetries of molecular and atomic electronic states for the reactants and products at infinite separation. The treatment of ozone dissociation by Valentini[48] is a specific example of this approach. To account for possible symmetry changes due to nuclear motion or isotopic substitution, a more detailed consideration of molecular symmetry is required. Quack[68] derived a general method for obtaining selection rules for the rovibronic states of molecules undergoing reactive collisions and explicitly discussed the problem of identical nuclei. He finds that the appropriate symmetry group not only includes the usual three-dimensional rotation−reflection group, but also permutations of the indices of identical nuclei of all reactants and products. As a result of this, in reactions involving identical nuclei, only certain rovibronic states of reactants and products can be connected, due to the requirement that the total Hamiltonian be invariant to operation of this larger permutation−inversion (PI) group. Gellene[69] extended this method and applied it specifically to the diatomic collisions of the type: $A_2 + A_2$, $A_2 + B_2$, or $AB + AB$. On the basis of the PI groups, a symmetry scheme was developed that connects the symmetry of the total wave function of the infinitely separated collision partners with the electronic symmetries of the system in the interaction region. Gellene concluded that a symmetry restriction may apply if (1) the two diatomic molecules are identical or (2) at least one of the molecules is in a degenerate electronic state. Case 1 is exemplified by the reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H \qquad (63)$$

and its isotopic modifications. The symmetry requirements in this case indicate that for the case of nonidentical collision partners (i.e., A_2/B_2^+ or A_2/AB^+), collisions with both odd and even values of the orbital angular momentum (L) are allowed. For collisions of the type A_2/A_2^+, only odd L collisions are allowed, while for AB/AB^+ collisions, only even L collisions are allowed. This would lead to the conclusion that, on a per collision basis, the reaction rate for identical molecules (either homo- or heteronuclear) would be one-half that for nonidentical collision partners. The experimental value, comparing H_2^+/H_2, D_2^+/D_2, and HD^+/HD with H_2^+/D_2 and D_2^+/H_2, is 0.60, in reasonable agreement with the prediction.

Another example is provided by the cluster formation

$$O_2^+ + O_2 + M \rightarrow O_4^+ + M\ (M = O_2 \text{ or rare gas}) \qquad (64)$$

described by Griffith and Gellene.[64] In this case, the symmetries are those for $^{32}O_2^+/^{32}O_2$,$^{32}O_2^+/^{34}O_2$, and $^{34}O_2^+/^{32}O_2$, as the oxygen used contained only the natural abundance of ^{18}O. The symmetry correlations indicate that for the AB^+/A_2 case, wave functions with all combinations of the quantum numbers N, $J-S$, and L correlate with the ground electronic state of the cluster. Hence, no symmetry restrictions apply to reactions of the heteronuclear diatomic *ion* but do apply to reactions of the heteronuclear *molecule* and to the all-^{16}O system. In fact, the observed intensity ratios at low electron energies are roughly 10 times the natural abundance ratio for the pair $^{65}O_4^+/^{64}O_4^+$ and $^{66}O_4^+/^{64}O_4^+$. On the other hand, the ratio $^{66}O_4^+/^{65}O_4^+$ is just the expected natural abundance ratio.

Recently, Gellene[70] discussed the isotopic fractionation in the formation of ozone in terms of these symmetry arguments. The question is whether these arguments apply to the first step of the formation mechanism, which is

$$O_2(^3\Sigma_g^-) + O(^3P) + M \rightarrow O_3^* + M \qquad (65)$$

where O_3^* represents a collision complex. No symmetry restrictions are predicted for collisions of O atoms and isotopically heteronuclear O_2 because all levels correlate with the ground state of ozone in this case. However, the ground state of ozone correlates only with $J-S =$ even states of $^{18}O^{18}O$ or $^{16}O^{16}O$ and $I =$ even and $J-S =$ even or $I =$ odd and $J-S =$ odd for $^{17}O^{17}O$ (f parity states). L can be either even or odd for all cases. The equilibrium population ratio for homonuclear diatomics is $e/f = 2/1$, producing an upper limit to isotopic enrichment of two for $^{49}O_{30}$ or $^{50}O_3$, large enough to account for the experimental results. However, the collision process may scramble e and f states, decreasing the enrichment accordingly. Gellene accounts for this by introducing an adjustable parameter β such that factors of $(1 + 2\beta)/3$, $(7 + 2\beta)/9$, and 1 apply to molecules containing one, two, or three different isotopes, respectively. Thus, the predicted isotopic enrichment is the same for $^{16}O^{16}O^{18}O$, $^{16}O^{17}O^{17}O$, $^{17}O^{17}O^{18}O$, and $^{16}O^{18}O^{18}O$. For the three possible homonuclear forms of ozone, the enrichment is smaller, and for $^{16}O^{17}O^{18}O$ it is larger. A value of $\beta = 0.78$ fits some of the data of Mauersberger et al.[21,45] reasonably well (Figure 3). However, this SIKIE model does not explain the large difference in the rate constants for $^{18}O + {}^{16}O^{16}O$ vs $^{16}O + {}^{18}O^{18}O$, which should have identical symmetry properties. In addition, recall that Yang and Epstein[35,36] observed much smaller values of the enrichment than did Mauersberger et al.

IV. Oxygen Isotopic Abundances in Atmospheric Gases

Although many of the atmospheric observations leading to measurements of isotope effects have not provided information about the effect of both ^{17}O and ^{18}O, the determination of the relative isotopic abundance of the ^{16}O and ^{18}O isotopologues in molecules that have been investigated in laboratory reactions is relevant to the discussion of mass-independent isotope effects.

In the laboratory experiments on isotope fractionation in chemical reactions, the choice of an isotopic standard is not important, since ultimately a comparison is made of the isotopic composition of a reactant and product or of the remaining reactant compared with the initial reactant. However, in the measurement of isotopic compositions of atmospheric gases, such an absolute standard becomes necessary and it is not always obvious how this has been chosen. In the infrared spectrophotometric measurements on ozone, intensities have been compared with those from standard atmospheric IR spectra, in which the oxygen isotope distribution is assumed to be the same as that for atmospheric oxygen. The mass spectrometric measurements also use oxygen as the standard. However, in the measurements on CO and CO_2, the standard is SMOW or VSMOW ($^{18}\delta = {}^{17}\delta \equiv 0‰$) with respect to which atmospheric oxygen has a value of $^{18}\delta = 23.5‰$.

A. Tropospheric Ozone

Krankowsky et al.[71] made mass spectrometric measurements on tropospheric urban ozone and found that $^{50}\delta$ is (91 ± 2)‰ and $^{49}\delta$ is (71 ± 3)‰, independent of the ozone mixing ratio. While the enrichment is not the same for mass 49 and mass 50, the ratio is 0.78, compared with the predicted mass-dependent value of 0.53. Johnston and Thiemens[72] examined ozone from three localities: La Jolla and Pasadena, CA, and White Sands Missile Range, NM (WSMR). Mass spectrometric analyses were made on the oxygen resulting from ozone decomposition, and the comparison is made to atmospheric oxygen. There is considerable scatter in the data from samples taken on different days, but there also appears to be a small difference between the average isotopic compositions of ozone from the three locations. A three-isotope plot of $^{17}\delta$ vs $^{18}\delta$ was fit by a linear equation of the form $^{17}\delta = A + B(^{18}\delta)$, and the following values (in per mil) were obtained:

	La Jolla	WSMR	Pasadena
mean $^{18}\delta$	82.3(6.7)	89.7(4.3)	86.1(5.6)
(mean $^{18}\delta$)/(mean $^{17}\delta$)	0.84	0.87	0.77
A	10 ± 11	−21 ± 27	19 ± 10
B	0.7 ± 0.1	1.1 ± 0.3	0.54 ± 0.1

The numbers in parentheses are standard deviations. The agreement with the urban tropospheric ozone measurements of Krankowsky et al.[71] is satisfactory. The authors attribute the differences in the $^{18}O/^{17}O$ values to differences in the NO_x concentration at the different localities; this is consistently very high in Pasadena and almost negligible at White Sands. A mass-dependent isotope effect on the $NO + O_3$ reaction could be the important variable, and the relative isotope effects could provide a way to measure transport and turnover.

B. Total Column Ozone

In principle, infrared measurements can distinguish between the symmetrical and unsymmetrical forms of $^{50}O_3$. In this way, Rinsland et al.[73] used solar absorption Fourier transform spectroscopy from Kitt Peak, AZ, to determine a column enrichment of (110 ± 110)‰ for $^{16}O^{16}O^{18}O$ and (50 ± 70)‰ for $^{16}O^{18}O^{16}O$. The error bars in these measurements are too large to indicate a difference between the symmetrical and unsymmetrical heavy molecules. The overall magnitude of the enrichment is similar to that observed for tropospheric ozone.[71,72] Irion et al.[74] made FTIR measurements at Table Mountain, CA, and determined an enrichment for $^{16}O^{16}O^{18}O$ of (170 ± 40)‰. They were unable to determine the corresponding value for the symmetric molecule because of interference by other lines in the spectrum. Meier and Notholt[75] made ground-based FTIR measurements in the Arctic (79° N), utilizing both solar absorption and lunar absorption spectra. The results are

	$^{16}O^{16}O^{18}O$	$^{16}O^{18}O^{16}O$
solar spectra	(154 ± 9)‰	(112 ± 14)‰
lunar spectra	(90 ± 33)‰	(85 ± 25)‰

The agreement between the Table Mountain value and the solar spectra value measured in the Arctic is quite good. Whether there is some significance to the lower values obtained from the lunar spectra during the Arctic night is not clear. The larger error bars associated with the latter data decrease the difference between the day and night values, but there may be an effect due to the absence of atmospheric photochemistry during the Arctic night.

C. Stratospheric Ozone

Mauersberger[10] was the first to report enrichment of $^{50}O_3$ in the stratosphere. Using a balloon-borne mass spectrometer, he observed values of $^{18}\delta$ as high as 400‰, which would be very difficult to understand on the basis of mass-dependent isotope effects. This report of such very large enrichments was doubtless a factor in initiating laboratory experiments designed to confirm the effect. At altitudes of 25−43 km, Mauersberger[76] found values ranging from about 200‰ to over 400‰, with large differences between the values obtained on two different balloon flights. Infrared emission spectroscopy was used by Abbas et al.,[77] who found enrichment that increased rapidly with altitude in the range of 25−37 km. Carli and Park[78] also used far-infrared emission spectroscopy but found relatively constant δ values of about 100‰ at altitudes of 28−45 km. Column-averaged ratios above 37 km were obtained from two balloon flights, using IR solar absorption spectroscopy.[79] Normalized to the standard isotopic ratios, enrichments of (180 ± 16)‰ for $^{16}O^{18}O^{16}O$ and (320 ± 22)‰ for $^{18}O^{16}O^{16}O$ were determined. Schueler et al.[80] used a method in which samples were taken at altitudes of about 30 km and later subjected to mass spectrometric analysis. They found enrichments of 80−160‰ for ^{18}O and were also able to observe $^{17}\delta$ values of about 80−110‰. Irion et al.[74] also report FTIR solar absorption spectra from shuttle flights at altitudes of 25−40 km (ATMOS), with measurements of both mass 50 isotopomers. The mass 50 enrichment was essentially independent of altitude, with an average value of (130 ± 50)‰. The individual values are $^{16}O^{16}O^{18}O$ = (150 ± 60)‰ and $^{16}O^{18}O^{16}O$ = (100 ± 70)‰. Within the rather wide error limits, these values do not seem significantly different from the total ozone column values, although they are higher than the values for tropospheric ozone.[71,72] This paper also presents a summary (their Figure 1) of the other stratospheric observations based on both mass spectrometric and FTIR techniques. Most of these overlap the ATMOS range of values, with the possible exceptions of the very large values (up to 400%) first reported by Mauersberger.[10,76]

Even before the first measurements were reported, Cicerone and McCrumb[81] suggested that heavy isotope enrichment of stratospheric ozone could result from the preferential photodissociation of $^{34}O_2$, owing to the self-shielding of solar UV radiation by the more prevalent $^{32}O_2$ species higher in the atmosphere. Blake et al.[82] later carried out a line-by-line calculation of the photodissociation yield and concluded that this effect was an order of magnitude smaller than was originally estimated. In any case, this explanation was made untenable by the calculations of Kaye and Strobel,[42] who showed that O-atom exchange reactions of the type

$$^{18}O + {}^{32}O_2 \rightleftarrows {}^{16}O + {}^{34}O_2 \qquad (66)$$

were rapid enough to scramble the oxygen isotopes, canceling any enhancement that would result from the preferential photodissociation of the heavy oxygen molecule. (In fact, Cicerone and McCrumb pointed this out in the final sentence of their paper.) Using only reactions involving oxygen species, i.e., O, O_2, and O_3, and literature values of rate constants together with values for the photolysis of oxygen and ozone, Kaye and Strobel show that the enrichment depends only on the equilibrium constant for the exchange process:

$$^{18}O + {}^{48}O_3 \rightleftarrows {}^{16}O + {}^{50}O_3, K_{eq} \qquad (67)$$

If f denotes the fraction of ^{18}O atoms in oxygen, the isotope ratio $[^{50}O_3]/[^{48}O_3]$ is given by $2f(1 + 2K_{eq})/K_{eq}$, compared with the statistical value $3f$. This ratio is found to be almost independent of altitude (depending only on the ambient temperature) and is ~0.96, indicating that the ozone should be *depleted* in the heavy isotope. Consideration of another possible exchange reaction, that between molecular oxygen and ozone, also indicates depletion.

Valentini[48] discusses the application of the symmetry effects observed in the ozone photodissociation to the problem of oxygen isotope fractionation in stratospheric ozone. However, the low concentration of $O(^3P)$ atoms makes the recombination slow with respect to electronic quenching of the $O_2(^1\Delta_g)$ molecules, and production of $O_2(^1\Delta_g)$ by the photolysis of ozone is also slow compared to the quenching rate. To account for an observed heavy isotope enrichment, some selective reaction involving $O_2(^1\Delta_g)$ is required and possible reaction mechanisms are discussed.

Arguments similar to those of Valentini were used by Miller et al.[83] in discussing another possible mechanism for the observations of heavy isotope enrichment in stratospheric ozone. Their work suggests that highly vibrationally excited oxygen ($X\,^3\Sigma_g^-$, $v \geq 26$) is produced in the UV photolysis of ozone. The vibrationally excited oxygen can react with molecular oxygen in the ground vibrational state:

$$O_2\,(X\,^3\Sigma_g^-, v \geq 26) + O_2 \rightarrow O_3 + O \qquad (68)$$

The symmetry argument implies that ozone containing either heavy isotope will undergo the curve-crossing process to form O_2 ($^3\Sigma_g$) more readily than will the $^{48}O_3$ molecule. Some of these heavy ozone molecules will dissociate to produce vibrationally excited O_2 which can react to form ozone. Thus, one of the O atoms in the original ozone is incorporated into a new ozone molecule without having undergone a reaction forming O atoms, hence, avoiding the O + O_3 mechanism. This slight nonrandomizing effect was shown by the authors to lead to increases in heavy ozone of 0.6−5.4% at altitudes of 40−55 km. However, heavy isotopic enrichment is actually observed at much lower altitudes, so this effect can only be a partial explanation of the observations. A second paper by Houston et al.[84] discusses this possible explanation in greater detail, and it is shown to lead to a heavy isotope enrichment by a factor of $1 + (f/3)n_{cycles}$, where f is the fraction of ozone dissociations leading to O_2 ($v \geq 26$) and n_{cycles} is the number of cycles in which ozone is formed from O and O_2 and dissociates. These calculations lead to a predicted maximum heavy isotope enrichment of about 30‰ at an altitude of 42 km, considerably smaller than the observed values.[74,76−80]

D. Stratospheric Carbon Dioxide

Gamo et al.[85] obtained carbon and oxygen isotopic ratios of carbon dioxide at altitudes of 5−25 km. They measured a slight increase with altitude in the mass 46 enrichment, which reached a maximum of about 43‰ relative to SMOW. Thiemens et al.[86] report on the oxygen isotopic composition of carbon dioxide collected during the same balloon flights in which ozone was collected.[80] By converting the oxygen of the carbon dioxide to molecular oxygen, they could measure the $^{17}O/^{16}O$ ratio, which was not possible for Gamo et al. because of interference by ^{13}C. Over the range of 25−35 km, there appears to be no altitude dependence of the enrichment, with an average value for mass 34 of about (50 ± 2)‰ relative to the SMOW standard. The enrichment of mass 33 was lower, with an average 33/34 ratio of 0.64 ± 0.04, compared to their measured ratio of 0.52 for carbon dioxide from the troposphere. This value is established by the oxygen exchange between carbon dioxide and water. More recently, Thiemens et al.[87] analyzed gas samples obtained cryogenically during four rocket flights. The samples were analyzed for CO_2, CO, CH_4, and N_2O, and $^{18}\delta$ and $^{17}\delta$ measurements were made for both oxygen and carbon dioxide. Both ^{17}O and ^{18}O enrichment in CO_2 increased slightly with altitude in the range of 30−60 km, and the $^{18}\delta$ values are comparable to those observed in the earlier paper.[85] The $^{17}\delta/^{18}\delta$ ratios in carbon dioxide average 0.69 ± 0.03, increasing slightly with altitude. The isotopic composition of the oxygen shows a very slight decrease in mass 46 at the higher altitudes, which the authors believe to be outside the limits of error in the measurements. The $^{17}\delta/^{18}\delta$ ratios in molecular oxygen are essentially those expected from mass-dependent fractionation. The isotopic fractionation between carbon dioxide and oxygen at a specific altitude is given by $\delta^n(CO_2) - \delta^n(O_2)$, and the ratio of the mass 45 to mass 46 enrichment ranges from 0.78 to 0.92, somewhat larger than the effect observed for carbon dioxide alone.

Thiemens et al.[88] recently reported simultaneous measurements of the oxygen isotope abundances and

^{14}C activity in carbon dioxide from samples taken at altitudes of 10−12 km and latitudes ranging from 52° to 85° S. The quantity $\Delta^{17}O \equiv {}^{17}\delta - 0.52({}^{18}\delta)$ appears to have a roughly linear correlation with $^{14}CO_2$, which the authors believe is an indication that the mass-independent isotope fractionation depends on intrusions of stratospheric air containing ^{14}C produced by cosmic ray bombardment of atmospheric nitrogen. The cause of the oxygen isotope effect in the stratosphere is believed to be exchange of carbon dioxide with $O(^1D)$ atoms, discussed previously in section IIID. However, it is worth noting that the average of the upper atmosphere measurements gives a ratio of 0.527 ± 0.002, while the cited error in the measurements leads to a propagated error in the ratio of 0.003. Another point of view might be that the agreement between this ratio and the mass-dependent ratio of 0.526 measured for tropospheric carbon dioxide is very good.

Yung et al.[89] carried out modeling calculations designed to account for the $^{18}OC^{16}O$ distribution in the lower stratosphere observed by Gamo et al.[85] They included the following mechanism in their model:

$$O_2Q + h\nu \rightarrow O_2 + Q(^1D) \tag{69}$$

$$Q(^1D) + M \rightarrow Q + M \tag{70}$$

$$Q(^1D) + CO_2 \rightarrow COQ + O \tag{71}$$

$$O(^1D) + COQ \rightarrow CO_2 + Q \tag{72}$$

$$O(^1D) + CQ \rightarrow CO + Q \tag{73}$$

$$Q(^1D) + CO \rightarrow CQ + O \tag{74}$$

$$(Q = {}^{16}O \text{ or } {}^{18}O)$$

The authors used a Caltech-JPL one-dimensional photochemical model for the necessary rate constants and concentrations as a function of altitude to calculate the ratio $C^{18}O^{16}O/C^{16}O_2$. The $^{18}\delta$ values assumed for ozone were based on the measurements of Mauersberger[10] as an upper limit, which is probably too high in view of more recent determinations. A better fit was obtained when one-third of this δ value was used in the model. The effect of doubling the eddy diffusion coefficients was to significantly reduce the ^{18}O enrichment at stratospheric altitudes, by increasing the mixing with tropospheric ozone which contains less ^{18}O. The model indicates that there is little or no change in $^{18}\delta$ up to about 15 km, in agreement with the measurements of both Gamo et al.[85] and Thiemens et al.[86−88] At the time these calculations were made there were no observations at higher altitudes (above ∼25 km), where the calculated effect is largest. However, the more recent measurements of Thiemens et al. show a rather wide scatter at 28−32 km that is centered around the calculated values with the greater eddy diffusion.

In a more recent paper, Yung et al.[56] combine what is essentially this same kinetic model with a one-dimensional atmospheric model to predict the ^{18}O distribution at higher altitudes. As in the case of the earlier calculations,[89] better agreement with observations was found if the eddy diffusion coefficient was increased by a factor of 2 times the normal value.

E. Atmospheric Nitrous Oxide

A new example of a mass-independent anomaly for oxygen isotopes has been reported recently by Cliff and Thiemens.[90] They determined $^{17}\delta$ and $^{18}\delta$ values in a large number of nitrous oxide samples obtained from four different sampling locations, all at the surface of the earth. A plot of $^{17}\delta$ vs $^{18}\delta$ over the range of $-22 < {}^{18}\delta < 20$ shows the expected mass-dependent ratio of $^{17}\delta = 0.515(^{18}\delta)$. However, on a larger-scale plot over a narrower range of $^{18}\delta \approx 16-20$, there is an observable offset from the line extrapolated from lower values of δ. If the deviation from the expected value is defined by $^{17}\Delta O$, values of about 1 per mil are obtained. Note that this effect is considerably smaller than that observed in several other cases in which $^{17}\delta \simeq {}^{18}\delta$. The same issue of *Science* contains an article by Yung and Miller,[91] in which the expected isotopic fractionation in the ultraviolet dissociation of N_2O is calculated, based on calculated spectral shifts resulting from differences in vibrational frequencies of the isotopologues. As a result of the larger cross section of the $^{14}N^{14}N^{16}O$ isotopologue for dissociation in the solar spectral region, calculated values of $^{18}\delta$ range from about 1 to 30 per mil over the altitude range of 20−60 km. However, the calculated spectral shift for the ^{17}ONN molecule is about one-half that of the ^{18}ONN molecule, and one would expect the calculated isotope effect to be given approximately by the usual mass-dependent ratio. It should be relatively simple for the authors to calculate this effect within the atmospheric model framework they use.

F. Tropospheric Carbon Monoxide

Measurements of oxygen isotope distributions in atmospheric CO have been reported recently.[11,12,59,92,93] Röckmann et al.[59] obtained tropospheric air samples at Alert, Canada (81° N) and Spitsbergen, Norway (81° N). A significant time dependence in the period from November to March is shown in both sets of samples, with an increase in CO concentration and $^{18}\delta$ and a decrease in $\Delta^{17}O$. The increasing CO concentration is probably the result of contributions during the winter from combustion sources, which have been shown to produce isotopically heavy CO. The decrease in $\Delta^{17}O$ is caused by dilution of CO subject to mass-independent effects with the mass-dependently fractionated combustion product. If it is assumed that the mass-independent fractionation is produced by ozonolysis of non-methane hydrocarbons (section IIIE), 10−15% of the total CO is derived from this source. Then the resulting input of $C^{18}O$ must be balanced by a depleted source of comparable strength. In the second paper on this subject,[12] the time dependence is extended to July and samples from Izaña, Tenerife, Canary Islands (28° N) are included for the period from November to April. The CO concentration and $^{18}\delta$ values from the high-latitude samples decrease from early spring to summer, and the $\Delta^{17}O$ values increase over this time period. The Tenerife data show relatively little seasonal dependence, and while [CO] and $^{18}\delta$ values are smaller than the high altitude values, $\Delta^{17}O$ is somewhat larger. This could be explained by a larger contribution from the OH + CO reaction relative to combustion sources. The OH sink is photochemically driven and would be more important at low latitudes during the winter months.

The oxygen isotopic measurements on atmospheric CO by Huff and Thiemens[11,93] were discussed in the Introduction.

V. Summary and Conclusions

(1) The number of independent investigations in which anomalous isotope effects involving light elements, particularly oxygen, have been observed rules out the possibility that such effects are due to experimental artifacts.

(2) In much of the reported work, the experiments are not described in sufficient detail for the actual magnitude of the isotope effects to be calculated. In many cases, there is the possibility of isotopic exchange between reactants and products, so that the observed effect may be some combination of kinetic and equilibrium isotope effects. The experiments by Sehested et al.[46] on the O + O_2 reaction are exemplary, because the oxygen atoms are produced by radiolysis of CO_2, and thus the isotopic composition of the dioxygen is not perturbed by the atom production process. It is to be hoped that similar experiments can be carried out with ^{17}O as well. In some cases where the data are sufficiently detailed to permit a calculation of the isotope effect, the individual ^{17}O and ^{18}O effects are of the order of magnitude expected from mass-dependent effects. However, the important observation is that the ^{17}O effect is approximately as large as the ^{18}O effect and not about one-half the effect of ^{18}O, as would be predicted by the theory of mass-dependent isotope effects.

(3) Many of the laboratory experiments involve either photochemical or electric discharge processes in which ions, electronically excited atoms, and electronically excited molecules are expected to be present. In addition, these systems are unlikely to be at thermodynamic equilibrium, so that the application of mass-dependent theory is not justified, except perhaps to provide a crude estimate of the anticipated isotope effects. These systems often show $^{17}\delta/^{18}\delta$ ratios that depend on the pressure of added inert gas or specific inert gas used. This effect has not been satisfactorily explained.

(4) On the other hand, the thermal decomposition of ozone is a well-understood reaction that involves only ground-state atoms and molecules. Under the conditions reported by Wen and Thiemens,[50,51] the mechanism simplifies to the unimolecular dissociation of ozone forming an oxygen atom and an oxygen molecule. Nevertheless, the anomalous relationship between $^{17}\delta$ and $^{18}\delta$ remains. This may be a system in which further experiments would be useful, in particular some type of spectroscopic observations of the reaction in real time, to avoid the complications of secondary reactions and isotopic exchange reactions involving reactants and products. As the experiments of Anderson et al.[24] indicate, tunable diode infrared laser absorption spectroscopy would be a suitably sensitive analytical technique, which has the advantage of distinguishing between structurally different molecules with the same molecular weight, such as $^{18}O^{16}O^{16}O$ and $^{16}O^{18}O^{16}O$. The drawback to this system is the fact that the ozone decomposition is very sensitive to catalysis by impurities and by surfaces.

Other more stable molecules with the requisite symmetry, such as CO_2 or SO_2, might be more amenable to experimental investigation. For example, although the $O(^1D) + CO_2$ exchange reaction has been studied fairly extensively, the comparison of ^{17}O and ^{18}O isotope effects was made under conditions where exchange of oxygen atoms with O_2 or O_3 is possible. A time-resolved kinetic experiment using the photolysis of N_2O as a stable source of $O(^1D)$ would be valuable. The OH + CO reaction is also an interesting case which does not have the disadvantages of reactions involving ozone. The kinetic isotope effects could also be studied in a time-resolved mode, using either tunable diode absorption spectrometry or mass spectrometric analysis.

(5) The laboratory experiments involving either ozone production or destruction produce much smaller isotope effects than the isotopic fractionation observed in samples of stratospheric ozone. The wide variation in the isotopic enrichment reported for stratospheric ozone suggests that sampling errors may be responsible for some of the large effects reported. Further observations are desirable. However, these measurements on atmospheric gases indicate the promise of using the mass-independent isotope effects as a means of determining the movement of air masses.

(6) From the very beginning of the work on anomalous isotope effects, the effect of molecular symmetry on the partition functions of isotopomers has been invoked as a source of the observed isotope fractionation. Bates[28,30−33] has argued convincingly that such effects cannot lead to isotopic fractionation, unless there is a difference in the two *apparently* equivalent bonds of a species such as $^{16}O{-}^{18}O{-}^{16}O$. This could result from formation in the reaction $^{16}O + ^{18}O^{16}O$, with more energy in the newly formed bond. The important question then becomes the rate of internal vibration relaxation relative to that of molecular dissociation.

On the other hand, Valentini[47,48] showed very directly that symmetry effects are important in the photolysis of ozone by using CARS spectroscopy to examine the distribution of rotational states of the O_2 ($^1\Delta$) product. The fact that the homonuclear molecule has only odd-J states, combined with selection rules for the possible curve crossing between O_2 ($^1\Delta_g$) + O (^1D) and O_2 ($^3\Sigma_g$) + O (^3P) leads to a depletion of heavy isotopes in O_2 ($^1\Delta_g$), as observed in the spectra. This explanation provides at least a qualitative explanation for the isotope effects in ozone photolysis and formation in an electric discharge and even indicates why the greatest effect is observed for the $^{16}O^{17}O^{18}O$ molecule.

Gellene[70] has approached the symmetry question in a somewhat different way that does not require the intervention of excited states or curve crossing of different states, and his method also predicts the relative effects for the several ozone isotopomers of mass 48–54. To make a quantitative comparison with observed enrichment values, in his method it is necessary to introduce an adjustable parameter that accounts for the collisional mixing of different symmetry species. This could presumably be done for the Valentini model as well.

If, indeed, the molecular symmetry of the reactants is the basis for anomalous isotope effects involving O_3, CO_2, and ion–molecule reactions, it cannot provide a basis for isotope effects observed in atmospheric nitrous oxide or in the CO + OH reaction. Indeed, as mentioned previously, even some of the ozone isotope effects are not explicable on the basis of molecular symmetry.

(7) The "mass-independent isotope effect story" will not be complete until one can predict the magnitude of such effects from a rigorously correct theoretical model. This is clearly not the case at the present time. Until such a goal has been reached, the utility of such effects in providing information about detailed reaction mechanisms or molecular properties is not evident, in contrast with the widespread use of mass-dependent effects. However, even with this limitation, observed mass-independent isotope effects may play an important role in modeling atmospheric chemical systems.

VI. Abbreviations and Acronyms

CARS: coherent anti-Stokes Raman spectroscopy

FTIR: Fourier transform infrared spectroscopy

Isotopologue: In accordance with the definitions adopted by the IUPAC, isotopologues are molecules differing in isotopic composition, such as $^{16}O^{16}O$ and $^{18}O^{16}O$

Isotopomers: Isotopologues that are structural isomers, i.e., $^{18}O^{16}O^{16}O$ and $^{16}O^{18}O^{16}O$

SIKIE: symmetry-induced kinetic isotope effects

SNOW: standard mean ocean water. Water used as a reference for hydrogen and oxygen isotopic composition in mass spectrometry, with values that are accepted as a standard

VSNOW: Vienna standard mean ocean water. A later standard for the same purpose

VII. Appendix

The kinetic isotope effect on rate constants for reactions of oxygen atoms with oxygen molecules, either to form ozone or to scramble atoms, can be formulated with the aid of eq 18. As an example, the ratio of rate constants k_Q/k_O required for the analysis of the experimental results of Anderson et al.[20] can be estimated in a slightly different way than the method used by these authors. In particular, it should be noted that they have omitted the ratio of frequencies for motion along the reaction coordinate that is called for by eq 18.

Table 4. Calculated Rate Constant Ratios for Ozone Formation at 296 K[a]

	$k(X + YZ)/k(O + OO)$	
	TS1[b]	TS2[b]
$Q+QQ+M \rightarrow Q_3 + M$	0.926	0.806
$Q+OO+M \rightarrow QOO+M$	1.025	0.986
$O+QQ+M \rightarrow OQQ+M$	0.892	0.813
$O+OQ+M \rightarrow OOQ+M$	$^1/_2$(0.947)	$^1/_2$(0.911)
$O+QO+M \rightarrow OQO+M$	$^1/_2$(0.942)	$^1/_2$(0.893)
$Q+OQ+M \rightarrow QOQ+M$	$^1/_2$(0.983)	$^1/_2$(0.903)
$Q+QO+M \rightarrow QQO+M$	$^1/_2$(0.929)	$^1/_2$(0.881)

[a] Q = ^{18}O, O = ^{16}O. [b] TS1 is the normal ozone molecule without the antisymmetric stretching mode, which is assumed to be the reaction coordinate. TS2 assumes that the two symmetric frequencies of the transition state have also disappeared.

We require the ratio of rate constants for the isotopic scrambling reactions

$$Q + O_2 \rightarrow O + OQ,\ k_Q \qquad (75)$$

$$O + Q_2 \rightarrow Q + OQ,\ k_O \qquad (76)$$

where in this case O = ^{16}O and Q = ^{18}O.

Neglecting tunneling effects, which is reasonable for heavy atoms such as oxygen, we can write according to eq 18

$$k_Q/k_O = (\nu^{\ddagger}{}_{QOO}/\nu^{\ddagger}{}_{OQQ}) f_{Q_2/O_2}/f^{\ddagger}{}_{OQQ/QOO} \qquad (77)$$

We now have to specify vibrational frequencies of the transition state, and we do what Anderson et al. apparently did, which is to assume that the transition state is the ozone molecule, except for the loss of the antisymmetric stretching mode, which becomes the reaction coordinate. The frequencies for most of the isotopologues of ozone are given in the references cited in the Anderson et al. paper, and the authors have indicated a reasonable way of interpolating to obtain the unmeasured frequencies of stretching vibrations for $^{18}O^{16}O^{16}O$ from the other isotopologues. Using the values for ν_1 and ν_2 of $^{18}O^{16}O^{16}O$ and $^{18}O^{18}O^{16}O$, we obtain $f^{\ddagger}{}_{QQO}/_{OOQ} = 1.0550$ at 296 K. The ratio of frequencies along the reaction coordinate is (1028.11/994.03) = 1.0343. For the oxygen molecule, the f value can be obtained from the paper by Urey;[3] at 296 K, it is 1.1728. Finally, combining these values we obtain $k_Q/k_O = 1.150$, differing insignificantly from the value of 1.156 obtained by Anderson et al. We have assumed that the transition state is the normal ozone molecule, and any assumption of weakened bonds in the transition state will lead to a smaller value of $f^{\ddagger}{}_{QQO}/_{OOQ}$ and a larger value of k_Q/k_O. In the limiting case where $f^{\ddagger}{}_{QQO}/_{OOQ}$ is unity, $k_Q/k_O = 1.213$, significantly smaller than the value of 1.256 these authors need to fit the enhancement of $^{18}O_3$ observed by Mauersberger et al.[45]

This same approach can be used to estimate isotope effects for all the ozone formation reactions, assuming that the transition state for this reaction is the same as that for isotopic scrambling. The results are shown in Table 4. The comparison with the experimental results of Table 3 is dissappointing, at best. The experimental ratios $k(X + YZ)/k(O + OO)$ are almost all greater than unity, whereas all but one of the calculated values is less than unity.

VIII. Acknowledgments

This work was carried out at Brookhaven National Laboratory under Contract DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. I thank Professor Jacob Bigeleisen for introducing me long ago to the study of isotope effects and for helpful comments on this paper.

IX. Note Added in Proof

New information about mass-independent isotope effects in the formation of ozone was presented at the *International Conference on Stable Isotopes and Isotope Effects* (Carry le Rouet, France, June 20−25, 1999). Additional experimental results presented by Jürgen Günther from the Mauersberger group (Heidelberg) answered some of the questions raised in section V of this paper. A new theoretical treatment[94] based on RRKM calculations of rate constants for the dissociation of the newly formed ozone molecule was presented by B. C. Hathorn and R. A. Marcus (California Institute of Technology). It is assumed that symmetry restrictions decrease the number of possible interactions and, hence, the density of states, such that non-RRKM (non-statistical) effects are present in the symmetrical adduct. Preliminary calculations give encouraging agreement with the results of Mauersberger et al.[21,37,45] T. A. Baker and G. I. Gellene (Texas Tech University) abandon altogether the idea that symmetry restrictions are responsible for the mass-independent isotope effects and instead propose a purely dynamic effect on the lifetimes of the different triatomic complexes. Semiclassical trajectory calculations produce relative rate constants that are in reasonable agreement with experimental results.

X. References

(1) Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, *15*, 261.
(2) Bigeleisen, J. *J. Chem. Phys.* **1949**, *17*, 675.
(3) Urey, H. C. *J. Chem. Soc.* **1947**, 562.
(4) Nier, A. O.; Ney, E. P.; Ingraham, M. G. *Rev. Sci. Instrum.* **1947**, *18*, 294.
(5) Bigeleisen, J.; Wolfsberg, M. *Adv. Chem. Phys.* **1958**, *1*, 16.
(6) *Isotopes and Chemical Principles*; Rock, P. A., Ed.; ACS Symposium Series II; American Chemical Society: Washington, DC, 1975.
(7) Melander, L.; Saunders, W. A., Jr. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York, 1980.
(8) *Isotope Effects in Gas-Phase Chemistry*; Kaye, J. A., Ed.; ACS Symposium Series 502; American Chemical Society: Washington, DC, 1992.
(9) Thiemens, M.; Heidenreich, J. E., III. *Science* **1983**, *219*, 1073. A more detailed version of this article appears as Heidenreich, J. E., III; Thiemens, M. H. *J. Chem. Phys.* **1983**, *78*, 892.
(10) Mauersberger, K. *Geophys. Res. Lett.* **1981**, *8*, 935.
(11) Huff, A. K.; Thiemens, M. H. *Geophys. Res. Lett.* **1998**, *25*, 3509.
(12) Röckmann, T.; Brenninkmeijer, C. A. M.; Saueressig, G.; Bergamaxchi, P.; Crowley, J. N.; Fischer, H.; Crutzen, P. J. *Science* **1998**, *281*, 544.
(13) Bigeleisen, J. *J. Am. Chem. Soc.* **1996**, *118*, 3676.
(14) Bigeleisen, J. *Proc. Int. Symp. Isot. Sep., 1st, 1957* **1958**, 121.
(15) Bigeleisen, J. In *Tritium in the Physical and Biological Sciences*; International Atomic Energy Agency: Vienna, 1962; Vol. I, p 161.
(16) Kotaka, M.; Okamoto, M.; Bigeleisen, J. *J. Am. Chem. Soc.* **1992**, *114*, 6436.
(17) Matsuhisa, Y.; Goldsmith, J. R.; Clayton, R. N. *Geochim. Cosmochim. Acta* **1978**, *42*, 173.
(18) Bigeleisen, J. Private communication, 1998.
(19) Anderson, S. M.; Klein, F. S.; Kaufman, F. *J. Chem. Phys.* **1985**, *83*, 1648.
(20) Anderson, S. M.; Hülsebusch, D.; Mauersberger, K. *J. Chem. Phys.* **1997**, *107*, 5385.
(21) Mauersberger, K.; Erbacher, B.; Krankowsky, D.; Günther, J.; Nickel, R. *Science* **1999**, *283*, 370.
(22) Morton, J.; Barnes, J.; Schueler, B.; Mauersberger, K. *J. Geophys. Res.* **1990**, *95*, 901.
(23) Kaye, J. A. *J. Geophys. Res.* **1986**, *91*, 7865.
(24) Heidenreich, J. E., III; Thiemens, M. H. *J. Chem. Phys.* **1986**, *84*, 2129.
(25) Bains-Sahota, S. K.; Thiemens, M. H. *J. Phys. Chem.* **1987**, *91*, 4370.
(26) Heidenreich, J. E., III; Thiemens, M. H. *Geochim. Cosmochim. Acta* **1985**, *49*, 1303.
(27) Herzberg, G. *Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*; Van Nostrand Reinhold: New York, 1966; pp 473−479.
(28) Thiemens, M. H.; Jackson, T. *Geophys. Res. Lett.* **1990**, *17*, 717.
(29) Bates, D. R. *Geophys. Res. Lett.* **1986**, *13*, 664.
(30) Anderson, S. M.; Kaye, J. A. *Geophys. Res. Lett.* **1987**, *14*, 91.
(31) Bates, D. R. *Geophys. Res. Lett.* **1987**, *14*, 94.
(32) Bates, D. R. *Geophys. Res. Lett.* **1988**, *15*, 13.
(33) Bates, D. R. *J. Chem. Phys.* **1990**, *93*, 8739.
(34) Thiemens, M. H. *Isotope Effects in Gas-Phase Chemistry*; In Kaye, J. A., Ed.; ACS Symposium Series 502; American Chemical Society: Washington, DC, 1992; pp 138−154.
(35) Yang, J.; Epstein, S. *Geochim. Cosmochim. Acta* **1987**, *51*, 2011.
(36) Yang, J.; Epstein, S. *Geochim. Cosmochim. Acta* **1987**, *51*, 2019.
(37) Morton, J.; Schueler, B.; Mauersberger, K. *Chem. Phys. Lett.* **1989**, *154*, 143.
(38) Margrave, J. L.; Polansky, R. B. *J. Chem. Educ.* **1962**, *39*, 335.
(39) Anderson, S. M.; Morton, J.; Mauersberger, K. *Chem. Phys. Lett.* **1989**, *156*, 175.
(40) Wessel Larsen, N.; Pedersen, T.; Sehested, J. *Int. J. Chem. Kinet.* **1991**, *23*, 331.
(41) Wessel Larsen, N.; Pedersen, T.; Sehested, J. In *Isotope Effects in Gas-Phase Chemistry*; Kaye, J. A., Ed.; ACS Symposium Series 502; American Chemical Society: Washington, DC, 1992; pp 167−180.
(42) Kaye, J. A.; Strobel, D. F. *J. Geophys. Res.* **1983**, *88*, 8447.
(43) Thiemens, M. H.; Jackson, T. *Geophys. Res. Lett.* **1987**, *14*, 624.
(44) Thiemens, M. H.; Jackson, T. *Geophys. Res. Lett.* **1988**, *15*, 639.
(45) Mauersberger, K.; Morton, J.; Schueler, B.; Stehr, J.; Anderson, S. M. *Geophys. Res. Lett.* **1993**, *20*, 1031.
(46) Sehested, J.; Nielsen, O. J.; Egsgaard, H.; Wessel Larsen, N.; Pedersen, T.; Christensen, L. K.; Wiegell, M. *J. Geophys. Res.* **1995**, *100*, 20979.
(47) Valentini, J. J.; Gerrity, D. P.; Phillips, D. L.; Nieh, J.-C.; Tabor, K. D. *J. Chem. Phys.* **1987**, *86*, 6745.
(48) Valentini, J. J. *J. Chem. Phys.* **1987**, *86*, 6757.
(49) Bhattacharya, S. K.; Thiemens, M. H. *Geophys. Res. Lett.* **1988**, *15*, 9.
(50) Wen, J.; Thiemens, M. H. *J. Geophys. Res.* **1991**, *96*, 10911.
(51) Wen, J.; Thiemens, M. H. *Chem. Phys. Lett.* **1990**, *172*, 416.
(52) Zaslowsky, J. A.; Urbach, H. B.; Leighton, F.; Wnuk, R. J.; Wojtowicz, J. A. *J. Am. Chem. Soc.* **1960**, *82*, 2682.
(53) Yamazaki, H.; Cvetanović, R. J. *J. Chem. Phys.* **1964**, *40*, 582.
(54) Baulch, D. H.; Breckenridge, W. H. *Trans. Faraday Soc.* **1966**, *62*, 2768.
(55) Wen, J.; Thiemens, M. H. *J. Geophys. Res.* **1993**, *98*, 12801.
(56) Yung, Y. L.; Lee, A. Y. T.; Irion, F. W.; DeMore, W. B.; Wen, J. *J. Geophys. Res.* **1997**, *102*, 10857.
(57) Bates, D. R. *J. Chem. Phys.* **1990**, *93*, 2158.
(58) Bhattacharya, S. K.; Thiemens, M. H. *Z. Naturforsch.* **1989**, *44a*, 435.
(59) Röckmann, T.; Brenninkmeijer, C. A. M.; Neeb, P.; Crutzen, P. *J. Geophys. Res.* **1998**, *103*, 1463.
(60) Stevens, C. M.; Kaplan, L.; Gorse, R.; Durkee, S.; Compton, M.; Cohen, S.; Bielling, K. *Int. J. Chem. Kinet.* **1980**, *12*, 935.
(61) Bains-Sahota, S. K.; Thiemens, M. H. *J. Chem. Phys.* **1989**, *90*, 6099.
(62) Colman, J. J.; Xu, X.; Thiemens, M. H.; Trogler, W. C. *Science* **1996**, *273*, 774.
(63) Lee, C. W.; Thiemens, M. H. *Abstracts of Papers*, 214th ACS National Meeting, Las Vegas, NV, Fall 1997; American Chemical Society: Washington, DC, 1997; 222.
(64) Griffith, K. S.; Gellene, G. I. *J. Chem. Phys.* **1992**, *96*, 4403.
(65) Gellene, G. I. *J. Phys. Chem.* **1993**, *97*, 34.
(66) Yoo, R. K.; Gellene, G. I. *J. Chem. Phys.* **1995**, *102*, 3227.
(67) Yoo, R. K.; Gellene, G. I. *J. Chem. Phys.* **1996**, *105*, 177.
(68) Quack, M. *Mol. Phys.* **1977**, 34, 477.
(69) Gellene, G. I. *J. Chem. Phys.* **1992**, *96*, 4387.
(70) Gellene, G. I. *Science* **1996**, *274*, 1344.
(71) Krankowsky, D.; Bartecki, F.; Klees, G. G.; Mauersberger, K.; Schellenback, K. *Geophys. Res. Lett.* **1995**, *22*, 1713.
(72) Johnston, J. C.; Thiemens, M. H. *J. Geophys. Res.* **1997**, *102*, 25395.
(73) Rinsland, C. P.; Malathy Devi, V.; Flaud, J.-M.; Camy-Peyret, C.; Smith, M. A. H.; Stokes, G. M. *J. Geophys. Res.* **1985**, *90*, 10719.

(74) Irion, F. W.; Gunson, M. R.; Rinsland, C. P.; Yung, Y. L.; Abrams, M. C.; Chang, A. Y.; Goldman, A. *Geophys. Res. Lett.* **1996**, *23*, 2377.

(75) Meier, A.; Notholt, J. *Geophys. Res. Lett.* **1996**, *23*, 551.

(76) Mauersberger, K. *Geophys. Res. Lett.* **1987**, *14*, 80.

(77) Abbas, M. M.; Guo, J.; Carli, B.; Mencaraglia, F.; Carlotti, M.; Nolt, I. G. *J. Geophys. Res.* **1987**, *92*, 13231.

(78) Carli, B.; Park, J. H. *J. Geophys. Res.* **1988**, *93*, 3851.

(79) Goldman, A.; Murcray, F. J.; Murcray, D. G.; Kosters, J. J.; Rinsland, C. P.; Flaud, J.-M.; Camy-Peyret, C.; Barbe, A. *J. Geophys. Res.* **1989**, *94*, 8467.

(80) Schueler, B.; Morton, J.; Mauersberger, K. *Geophys. Res. Lett.* **1990**, *17*, 1295.

(81) Cicerone, R. J.; McCrumb, J. L. *Geophys. Res. Lett.* **1980**, *7*, 251.

(82) Blake, A. J.; Gibson, S. T.; McCoy, D. G. *J. Geophys. Res.* **1984**, *89*, 7277.

(83) Miller, R. L.; Suits, A. G.; Houston, P. L.; Toumi, R.; Mack, J. A.; Wodtke, A. *Science* **1994**, *265*, 1831.

(84) Houston, P. L.; Suits, A. G.; Toumi, R. *J. Geophys. Res.* **1996**, *101*, 18829.

(85) Gamo, T.; Tsutsumi, M.; Sakai, H.; Nakazawa, T.; Tanaka, M.; Honda, H.; Kubo, H.; Itoh, T. *Tellus* **1989**, *41B*, 127.

(86) Thiemens, M. H.; Jackson, T.; Mauersberger, K.; Schueler, B.; Morton, J. *Geophys. Res. Lett.* **1991**, *18*, 669.

(87) Thiemens, M. H.; Jackson, T. L.; Brenninkmeijer, C. A. M. *Geophys. Res. Lett.* **1995**, *22*, 255.

(88) Thiemens, M. H.; Jackson, T.; Zipf, E. C.; Erdman, P. W.; van Egmond, C. *Science* **1995**, *270*, 969.

(89) Yung, Y. L.; DeMore, W. B.; Pinto, J. P. *Geophys. Res. Lett.* **1991**, *18*, 13.

(90) Cliff, S. S.; Thiemens, M. H. *Science* **1997**, *278*, 1774.

(91) Yung, Y. L.; Miller, C. E. *Science* **1997**, *278*, 1778.

(92) Hodder, P. S.; Brenninkmeijer, C. A. M.; Thiemens, M. H. *Mass Independent Fractionation in Troposheric Carbon Monoxide*; Lanphere, M. A., Dalrymple, G. B., Turrin, B. D., Eds.; Abstracts of the 8th International Conference on Geochronology, Cosmochronology, and Isotope Geology, Circular, C 1107, Berkeley, CA, June 5−11, 1994; p 138.

(93) Huff, A. K.; Thiemens, M. H. *Eos Trans. AGU, Fall Meet. Supl.* **1996**, *77* (46), F124.

(94) Hathorn, B. C.; Marcus, R. A. *J. Chem. Phys.*, submitted for publication.

CR9800154