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Equilibrium thermodynamics of multiply substituted isotopologues of molecular gases

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Abstract—Isotopologues of molecular gases containing more than one rare isotope (multiply substituted isotopologues) can be analyzed with high precision ($1\sigma < 0.1‰$), despite their low natural abundances (~ ppm to ppt in air), and can constrain geochemical budgets of natural systems. We derive a method for calculating abundances of all such species in a thermodynamically equilibrated population of isotopologues, and present results of these calculations for O_2, CO, N_2, NO, CO_2, and N_2O between 1000 and 193 to 77 K. In most cases, multiply substituted isotopologues are predicted to be enriched relative to stochastic (random) distributions by ca. 1 to 2‰ at earth-surface temperatures. This deviation, defined as Δ_i for isotopologue i, generally increases linearly with 1/T at temperatures $\leq$ 500 K. An exception is N_2O, which shows complex temperature dependences and 10's of per-mill enrichments or depletions of abundances for some isotopologues. These calculations provide a basis for discriminating between fractionations controlled by equilibrium thermodynamics and other sorts of isotopic fractionations in the budgets of atmospheric gases. Moreover, because abundances of multiply substituted isotopologues in thermodynamically equilibrated populations of molecules vary systematically with temperature, they can be used as geothermometers. Such thermometers are unusual in that they involve homogeneous rather than heterogeneous equilibria (e.g., isotopic distribution in gaseous CO_2 alone, rather than difference in isotopic composition between CO_2 and coexisting water). Also, multiple independent thermometers exist for all molecules having more than one multiply substituted isotopologue (e.g., thermometers based on abundances of $^{18}O^{13}C^{16}O$ and $^{18}O^{12}C^{18}O$ are independent); thus, temperatures estimated by this method can be tested for internal consistency. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

Stable isotope geochemistry is principally concerned with bulk isotopic compositions of natural materials (e.g., $\delta^{13}C$ or $\delta^{18}O$ values). In gases, these bulk compositions effectively only depend on abundances of molecules containing one rare isotope (hereafter referred to as singly substituted isotopologues; e.g., $^{13}C^{16}O_2$ or $^{18}O^{12}C^{16}O$). However, there also exist molecules having more than one rare isotope (hereafter referred to as multiply substituted isotopologues; e.g., $^{18}O^{13}C^{16}O$). Urey (1947) and Bigeleisen and Mayer (1947) recognized that multiply substituted isotopologues have unique thermodynamic properties, different from both isotopically normal and singly substituted isotopologues of the same molecule. Similarly, the kinetic theory of gases predicts that multiply substituted isotopologues undergo distinctive fractionations during processes such as diffusion or gravitational settling (Present, 1958; Kaye, 1987; and references therein), and it seems likely to us that they also exhibit distinctive kinetic fractionations during metabolic or photochemical reactions. It follows that distributions of multiply substituted isotopologues in nature could provide unique constraints on geological, geochemical, and cosmochemical processes. Similar statements could be made about distributions of rare isotopes within condensed phases, although calculation and analysis of such isotopic "clumps" involve several difficulties beyond those encountered with gaseous molecules. We intend to address them in the near future, but consider them beyond the scope of this paper.

The geochemistry of singly substituted stable isotopologues is a large and diverse field, but virtually nothing is known about the natural abundances of their multiply substituted relatives. We suspect this is because commonly available gas-source mass spectrometers do not provide meaningful measurements of abundances of these very rare species and, in the absence of such data, there has been little incentive to explore their geochemistry. Eiler and Schauble (2004) report precise (sub-0.1‰) measurements of synthetic and atmospheric $^{18}O^{13}C^{16}O$ at natural isotopic abundances. These data both document the existence of anomalies and variations in abundances of multiply substituted isotopologues, and, more generally, demonstrate a set of techniques that could also be used to study multiply substituted O_2, N_2, CO, NO, N_2O, and perhaps other gases. These techniques do not appear to be appropriate for precise analysis of multiply deuterated molecules (e.g., D_2 or CH_2D_2). Therefore, although such analyses might become possible in the future, we will not consider these species in this study.

Theory describing partition functions of multiply substituted isotopologues was derived long ago (Bigeleisen and Mayer, 1947; Urey, 1947), but has not been systematically evaluated. This theoretical framework is a prerequisite for applied study because it provides a context for interpreting measured abundances of these species. This theory is particularly useful for recognizing and interpreting isotopic variations caused by equilibrium thermodynamics, much as calculations by Richet et al. (1977) provide a context for interpreting differences in bulk stable isotope composition between different molecular gases. In this paper, we develop a method for calculating the relative abundances of all stable isotopologues of molecular gases based on principles of statistical thermodynamics and various matrix algebra operations. We also combine that method with

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existing spectroscopic data to calculate expected abundances of isotopologues of thermodynamically equilibrated populations of N_2, O_2, CO, NO, CO_2, and N_2O between 1000 and 193 to 77 K.

2. METHODOLOGY

To calculate the abundances of all isotopologues of a given molecule at thermodynamic equilibrium and a specified temperature, we: (1) define the set of possible isotopologues for that molecule; (2) select a subset of these isotopologues that can uniquely define the bulk isotopic composition of a given population of molecules (e.g., its $^{18}O/^{16}O$ ratio, including contributions from all isotopologues); (3) define the set of independent isotope exchange reactions between all isotopologues; (4) use principles of statistical thermodynamics to evaluate the equilibrium constants of those reactions as functions of temperature (Bigeleisen and Mayer, 1947; Richet et al., 1977; O'Neil, 1986); and, finally, (5) calculate the proportions of all possible isotopologues that are consistent with both the bulk isotopic composition and the calculated equilibrium constants. Most steps of this algorithm make use of widely known mathematical principles and are defined and illustrated by example in section 2.1. Evaluation of equilibrium constants (step 4) involves principles of physical chemistry that are less widely understood and are described separately in section 2.2.

2.1. Algorithm

It is relatively straightforward to calculate the abundances of multiply substituted isotopologues of diatomic molecules of elements having only two isotopes. For example, there is only one isotope exchange reaction involving the three stable isotopologues of molecular nitrogen:

$$^{14}N^{14}N + {}^{15}N^{15}N \overset{K}{\rightleftharpoons} 2\,{}^{14}N^{15}N \qquad (1)$$
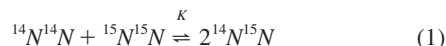
and, at equilibrium, proportions of these three isotopologues are uniquely defined by: the equilibrium constant for this reaction (K), the known bulk isotopic composition of that population (i.e., its $^{15}N/^{14}N$ ratio), and the equations describing isotopic mass balance in this system (i.e., $n_{14_N} = n_{14_N 15_N} + 2 n_{14_N 14_N}$, and $n_{15_N} = n_{14_N 15_N} + 2 n_{15_N 15_N}$, where n_i is the number of molecules of isotopologue i).

However, molecules containing three or more atoms and/or containing elements with more than two isotopes have several independent isotope exchange reactions, each of which has an equilibrium constant that constrains the proportions of isotopologues. These systems also have only one possible distribution of isotopologues when thermodynamically equilibrated at a given temperature, but that distribution is less easy to infer by inspection. We developed a method for handling such systems based on Gauss-Jordan reduction of a matrix. This method is inspired by composition-space analysis commonly used in petrology (Thompson, 1982).

We first project isotopic composition of every isotopologue of a molecule of interest into the composition space defined by the isotopes that molecule can contain. Figure 1a and b illustrates examples of projections of isotopologues of
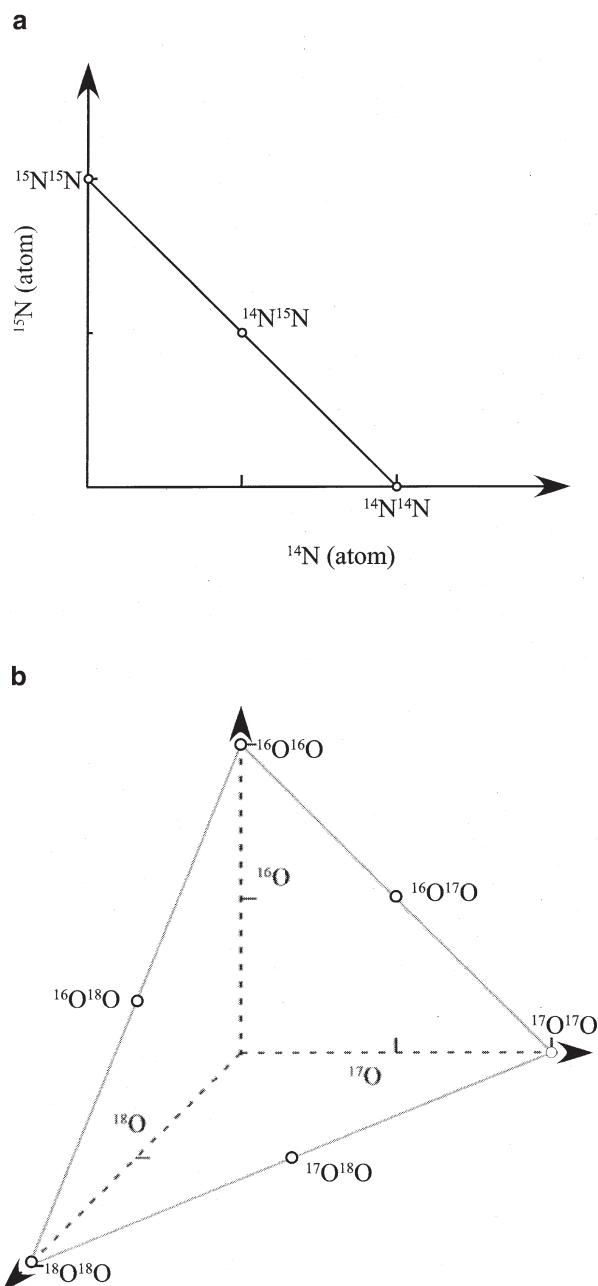

Fig. 1. (a) Projection of the compositions of isotopologues of N_2 into the composition space ^{14}N-^{15}N; note all isotopologues of N_2 lie on a straight line. (b) Projection of compositions of isotopologues of O_2 into the composition space ^{16}O-^{17}O-^{18}O; note all isotopologues of O_2 lie on a plane.

N_2 into the composition space ^{14}N-^{15}N and of O_2 into the composition space ^{16}O-^{17}O-^{18}O. Molecules containing five or more isotopologues (e.g., CO, NO, CO_2, and N_2O) cannot easily be illustrated in such plots but follow the same principles. All such projections can be formulated as matrices of simultaneous linear equations. For example, the stable isotopes making up CO_2, ^{12}C, ^{13}C, ^{16}O, ^{17}O, and ^{18}O can be used to define a five end-member composition space, and the twelve possible isotopologues of CO_2 can be projected into

that space using the set of linear equations making up the following matrix:

$$
\begin{pmatrix}
^{16}O & ^{12}C & ^{16}O \\
^{16}O & ^{13}C & ^{16}O \\
^{16}O & ^{12}C & ^{17}O \\
^{16}O & ^{12}C & ^{18}O \\
^{16}O & ^{13}C & ^{17}O \\
^{17}O & ^{12}C & ^{17}O \\
^{16}O & ^{13}C & ^{18}O \\
^{17}O & ^{12}C & ^{18}O \\
^{17}O & ^{13}C & ^{17}O \\
^{18}O & ^{12}C & ^{18}O \\
^{17}O & ^{13}C & ^{18}O \\
^{18}O & ^{13}C & ^{18}O
\end{pmatrix}
=
\begin{pmatrix}
1 & 0 & 2 & 0 & 0 \\
0 & 1 & 2 & 0 & 0 \\
1 & 0 & 1 & 1 & 0 \\
1 & 0 & 1 & 0 & 1 \\
0 & 1 & 1 & 1 & 0 \\
1 & 0 & 0 & 2 & 0 \\
0 & 1 & 1 & 0 & 1 \\
1 & 0 & 0 & 1 & 1 \\
0 & 1 & 0 & 2 & 0 \\
1 & 0 & 0 & 0 & 2 \\
0 & 1 & 0 & 1 & 1 \\
0 & 1 & 0 & 0 & 2
\end{pmatrix}
\begin{pmatrix}
^{12}C \\
^{13}C \\
^{16}O \\
^{17}O \\
^{18}O
\end{pmatrix}
$$

$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow$$
$$M \qquad\qquad\quad C \qquad\qquad\quad A$$

$$(2)$$

We define C here as the transformation matrix, M as the molecular species matrix and A as the isotope component matrix. Equation (2) can be simplified to:

$$E \cdot M = C \cdot A \qquad (3)$$

where E is 12×12 unit matrix.

The rank and dimensionality of matrix C define the set of linearly independent isotopologues needed to describe the bulk isotopic composition of the population; this set of isotopologues is referred to as the system components. The number of these system components always equals the number of isotopes contributing to a pool of isotopologues minus 1 (i.e., 4 in the case of the stable isotopes of CO_2), although several different choices of these four system components are possible, and the choice of a preferred set is arbitrary and does not affect the final calculation result. However, we believe it is least confusing to use isotopically normal and singly substituted isotopologues as the system components because these species are the most abundant and familiar, and they control the bulk isotopic compositions. We can select the preferred set of independent isotopologues by placing them in the first four positions of matrix M; subsequent matrix operations will identify these as the system components, as illustrated below. We diagonalize matrix C using Gauss-Jordan reduction and document the necessary operations in matrix E. This can be done by hand or using PLU decomposition—a tool included in several commercial software packages, including MAPLE or MATLAB. Any $m \times n$ real matrix can be decomposed as the product of PLU (where P is a permutation $m \times m$ matrix, L is a real lower triangular $m \times m$ matrix with 1 as each diagonal element, and U is an upper triangular $m \times n$ matrix). The result is expressed as follows:

$$C = PLU \qquad (4)$$

Because matrices P and L are invertible, we can multiply both sides of the Eqn. 3 by their inverses to find:

$$(PL)^{-1} \cdot M = U \cdot A \qquad (5)$$

The rank of the characteristic matrix, U, equals the rank of matrix C, and therefore, the number of system components that define the bulk isotopic composition of the population. More-

over, the locations of non-0 rows in matrix U correspond to the location of those system components in matrix M. The first n rows (counting from the top, where n equals the rank of matrix U) in matrices $(PL)^{-1}$ and U define the relationships between system components and isotope components; the remaining rows of matrix $(PL)^{-1}$ contain the stoichiometric coefficients for isotopologues in the set of linearly independent isotope exchange reactions for this molecule.

In the case of CO_2, the matrix $(PL)^{-1}$ and matrix U are

$$(PL)^{-1}$$

$$
=
\begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & -1 & -1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & -2 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & -1 & 0 & -1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & -1 & -1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
2 & -1 & -2 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
1 & 0 & 0 & -2 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
2 & -1 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
2 & -1 & 0 & -2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}
$$

$$(6)$$

$$
U =
\begin{pmatrix}
1 & 0 & 2 & 0 & 0 \\
0 & 1 & 2 & 0 & 0 \\
0 & 0 & -1 & 1 & 0 \\
0 & 0 & 0 & -1 & 1 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0
\end{pmatrix}
\qquad (7)
$$

In this case, the rank of U is four, indicating that the rank of the transformation matrix C is four, that four independent isotopologues are needed to describe the bulk composition of this system (as expected), and that they are the first four isotopologues in matrix M ($^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$, $^{16}O^{12}C^{17}O$, and $^{16}O^{12}C^{18}O$). The independent exchange reactions are defined by the bottom eight rows of matrix $(PL)^{-1}$ (i.e., excluding the first four rows—the rank of matrix U); these reactions can be expanded as follows:

row 5 :

$$^{16}O^{12}C^{16}O + {}^{16}O^{13}C^{17}O \overset{K_1}{\rightleftharpoons} {}^{16}O^{13}C^{16}O + {}^{16}O^{12}C^{17}O \quad K_1 = \frac{x_2 x_3}{x_1 x_5}$$

$$(8i)$$

row 6 :

$$^{16}O^{12}C^{16}O + {}^{17}O^{12}C^{17}O \overset{K_2}{\rightleftharpoons} 2\,{}^{16}O^{12}C^{17}O \quad K_2 = \frac{x_3^2}{x_1 x_6} \quad (8\text{ii})$$

row 7 :

$$^{16}O^{12}C^{16}O + {}^{16}O^{13}C^{18}O \overset{K_3}{\rightleftharpoons} {}^{16}O^{13}C^{16}O$$
$$+ {}^{16}O^{12}C^{18}O \quad K_3 = \frac{x_2 x_4}{x_1 x_7} \quad (8\text{iii})$$

row 8 :

$$^{16}O^{12}C^{16}O + {}^{17}O^{12}C^{18}O \overset{K_4}{\rightleftharpoons} {}^{16}O^{12}C^{17}O$$
$$+ {}^{16}O^{12}C^{18}O \quad K_4 = \frac{x_3 x_4}{x_1 x_8} \quad (8\text{iv})$$

row 9 :

$$2\,{}^{16}O^{12}C^{16}O + {}^{17}O^{13}C^{17}O \overset{K_5}{\rightleftharpoons} {}^{16}O^{13}C^{16}O$$
$$+ 2\,{}^{16}O^{12}C^{17}O \quad K_5 = \frac{x_4^2}{x_1 x_{10}} \quad (8\text{v})$$

row 10 :

$$^{16}O^{12}C^{16}O + {}^{18}O^{12}C^{18}O \overset{K_6}{\rightleftharpoons} 2\,{}^{16}O^{12}C^{18}O \quad K_6 = \frac{x_4^2}{x_1 x_{10}} \quad (8\text{vi})$$

row 11 :

$$2\,{}^{16}O^{12}C^{16}O + {}^{17}O^{13}C^{18}O \overset{K_7}{\rightleftharpoons} {}^{16}O^{13}C^{16}O$$
$$+ {}^{16}O^{12}C^{17}O + {}^{16}O^{12}C^{18}O \quad K_7 = \frac{x_2 x_3 x_4}{x_1^2 x_{11}} \quad (8\text{vii})$$

row 12 :

$$2\,{}^{16}O^{12}C^{16}O + {}^{18}O^{13}C^{18}O \overset{K_8}{\rightleftharpoons} {}^{16}O^{13}C^{16}O$$
$$+ 2\,{}^{16}O^{12}C^{18}O \quad K_8 = \frac{x_4^2 x_2}{x_1^2 x_{12}} \quad (8\text{viii})$$

where K_i indicates the equilibrium constant for exchange reaction i, and i equals the row number minus four. Assuming ideal mixing of all isotopologues of a given molecule, equations relating K_i to the mole fractions of reactant and product isotopologues are given next to each reaction, where x_j is the mole fraction of the isotopologue in row j of matrix M (e.g., x_1 is the mole fraction of $^{16}O^{12}C^{16}O$).

Given known values of K_i for all independent isotope exchange reactions (calculated in section 2.2, below), one need only define the mole fractions of the system components (i.e., $^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$, $^{16}O^{12}C^{17}O$, and $^{16}O^{12}C^{18}O$ for our example) to solve the set of eight nonlinear equations, Eqn. 8i through 8viii, and thereby retrieve the mole fractions of all dependent isotopologues. The mole fractions of the system components can be calculated based on independently defined bulk concentrations of isotopes in the population of isotopologues being considered (e.g., concentrations of ^{13}C, ^{12}C, ^{16}O, ^{17}O, and ^{18}O spread among all isotopologues of CO_2 for our

example) and the known K_i values. We do so by simultaneous solution of a number of mass balance equations equal to the number of system components (i.e., four mass balance equations for our example). These mass-balance equations are of two kinds: (1) one stipulating that the sum of mole fractions of all isotopologues equals one (i.e., $\sum_{i=1}^n x_i = 1$, summed over all n isotopologues; e.g., $n = 12$ for our example); and (2) several stipulating that the sum of mole fractions of all isotopologues containing a given isotope, multiplied by the stoichiometric coefficient for that isotope in that isotopologue (e.g., two for ^{16}O in $^{16}O^{13}C^{16}O$), equals the known concentration of that isotope in the entire population of isotopologues. n-1 independent equations of this second type are needed, where n equals the number of system components (e.g., constraints of this second type provide n-1 independent equations, where n equals the number of system components). For our example, the resulting four equations are:

$$x_2 + \frac{x_2 x_3}{K_1 x_1} + \frac{x_2 x_4}{K_3 x_1} + \frac{x_2 x_3^2}{K_5 x_1^2} + \frac{x_2 x_3 x_4}{K_7 x_1^2} + \frac{x_2 x_4^2}{K_8 x_1^2} = x_{13_C} \quad (9\text{i})$$

$$2x_1 + 2x_2 + x_3 + x_4 + \frac{x_2 x_3}{K_1 x_1} + \frac{x_2 x_4}{K_3 x_1} = 2x_{16_O} \quad (9\text{ii})$$

$$x_4 + \frac{x_2 x_4}{K_3 x_1} + \frac{x_3 x_4}{K_4 x_1} + \frac{2x_4^2}{K_6 x_1} + \frac{x_2 x_3 x_4}{K_7 x_1^2} + \frac{2x_2 x_4^2}{K_8 x_1^2} = 2x_{18_O}$$
$$(9\text{iii})$$

$$x_1 + x_2 + x_3 + x_4 + \frac{x_2 x_3}{K_1 x_1} + \frac{x_3^2}{K_2 x_1} + \frac{x_2 x_4}{K_3 x_1} + \frac{x_3 x_4}{K_4 x_1} + \frac{x_2 x_3^2}{K_5 x_1^2}$$
$$+ \frac{x_4^2}{K_6 x_1} + \frac{x_2 x_3 x_4}{K_7 x_1^2} + \frac{x_2 x_4^2}{K_8 x_1^2} = 1 \quad (9\text{iv})$$

For the special case that each value of K_i equals the mass-action constant for the relevant balanced reaction (e.g., when K_i values for Eqn. 8i through 8viii are 1, 4, 1, 2, 4, 4, 2, and 4, respectively), the exact solution for Eqn. 9i through 9iv is that the concentration of each of the system components equals the product of the concentrations of the isotopes it contains (e.g. $x_1 = x_{12_C} x_{16_O}^2$, $x_3 = 2x_{16_O} x_{12_C} x_{17_C}$). This is referred to as the stochastic or random distribution and corresponds to the expected distribution at infinite temperature. For the general case that K_i values are controlled by enhanced thermodynamic stabilities of certain isotopologues relative to others and differ from the stochastic distribution, we solve Eqn. 9i through 9iv numerically using line search procedures and a quasi-Newton method (also called the variable metric method). Programs for such numerical procedures can be found in Numerical Recipes (e.g., Press et al., 2002, chapter 10.1 and 10.7) or MATLAB (referring to MATLAB help files).We recommend using the concentrations of isotopologues corresponding to the stochastic distributions as initial guesses for these numerical solutions; other choices will yield the same result, just more slowly.

To test the precision of our numerical methods for solving Eqn. 9i through 9iv, we calculated the concentration of each isotopologue of CO_2 for a population having the stochastic distribution of isotopes using both: (1) the exact solution, and (2) the numerical method in which the initial guess for concentrations of independent isotopologues differed greatly from the stochastic distribution

(i.e., so that the numerical algorithm must converge on the final result from a highly aberrant initial condition). Differences between these two methods, defined as $\left(\dfrac{x_{numeric}}{x_{exact}} - 1\right)$, are less then 5.0×10^{-13} for all twelve CO_2 isotopologues for assumed bulk isotopic compositions within the natural range. This error is trivial compared to the variations in expected abundances of isotopologues calculated in section 3.

2.2. Evaluation of Equilibrium Constants

In this section we describe how equilibrium constants (K_i values) can be evaluated using classical statistical thermodynamics and spectroscopic data. We frame our discussion around calculation of the equilibrium constant for the isotope exchange reaction 8iii above, which involves isotopologue $^{18}O^{13}C^{16}O$, data for which is reported by Eiler and Schauble (2004). The same principles apply to other isotope exchange reactions of CO_2 and other gases discussed in section 3 of this paper.

The equilibrium constant of isotope exchange reaction 8iii, K_3, can be expressed as

$$K_3 = \frac{Q_{^{16}O^{13}C^{16}O} \cdot Q_{^{16}O^{12}C^{18}O}}{Q_{^{16}O^{12}C^{16}O} \cdot Q_{^{16}O^{13}C^{18}O}} \tag{10}$$

where Q_i is partition function for each isotopologue, i. Each partition function, Q_i, in this equation is the product of translational, vibrational (including zero point), and rotational energies, the rotation-vibration interaction energy, and electronic energy. For isotope exchange reactions involving molecules in the ground state, the electronic energy is ignored if one adopts the Born-Oppenheimer approximation (as we do), because it is independent of isotopic mass. Thus, only terms associated with the energies of translation, rotation and vibration need be considered. Urey (1947) presented a simplified calculation of the components of the partition function that are most important for isotope exchange reactions. He only considered the vibrational energy, approximated intramolecular bonds as harmonic oscillators, and adopted the Teller-Redlich product rule. Urey's solution for polyatomic molecules, stated in terms relevant for evaluation of the partition function ratio, $\dfrac{Q_{^{16}O^{13}C^{16}O}}{Q_{^{16}O^{12}C^{16}O}}$ (as an example), is:

$$\left(\frac{Q_{^{16}O^{13}C^{16}O}}{Q_{^{16}O^{12}C^{16}O}}\right)$$

$$= \frac{\sigma_{^{16}O^{12}C^{16}O}}{\sigma_{^{16}O^{13}C^{16}O}} \prod_{i=1}^{3n-5} \frac{u_i^{^{16}O^{13}C^{16}O}}{u_i^{^{16}O^{12}C^{16}O}} \frac{e^{-\frac{u_i^{^{16}O^{13}C^{16}O}}{2}}}{1 - e^{-u_i^{^{16}O^{13}C^{16}O}}} \frac{1 - e^{-u_i^{^{16}O^{12}C^{16}O}}}{e^{-\frac{u_i^{^{16}O^{12}C^{16}O}}{2}}} \tag{11}$$

where $\sigma_{^{16}O^{12}C^{16}O}$ and $\sigma_{^{16}O^{13}C^{16}O}$ are symmetry numbers of $^{16}O^{12}C^{16}O$ and $^{16}O^{13}C^{16}O$ (both equal 2), n is the number of atoms in the molecule of interest (both equal 3), $u_i = \dfrac{hc\varpi_i}{kT}$ (ϖ_i is the normal vibrational wave number for $^{16}O^{12}C^{16}O$ or

$^{16}O^{13}C^{16}O$ at each vibrating mode i; h is Plank's constant; c is light speed; k here is Boltzmann constant; T is absolute temperature). There are $3n$-6 normal vibrational modes for nonlinear polyatomic molecules, while there are only $3n$-5 for linear polyatomic molecules such as CO_2 and N_2O because the bending vibrational mode is doubly degenerate. Note that a factor of $\prod_i^n m_i^{\frac{3}{2}}$ (where m_i is the mass of atom i of n atoms that form the molecule) for each molecule is omitted in this expression because this factor will be eventually cancelled out when calculating equilibrium constants (refer to Davidson (1962)). Expressions having the form of Eqn. 11 have been widely used to predict equilibrium constants of isotope exchange reactions among gaseous species, and their temperature dependence (e.g., Richet et al., 1977). The equilibrium constant of isotope exchange reaction such as 8i through 8viii can be calculated by combining two or more expressions having the form of Eqn. 11. For example, K_3 equals the product of two partition function ratios, $\left(\dfrac{Q_{^{16}O^{13}C^{16}O}}{Q_{^{16}O^{12}C^{16}O}}\right) \cdot \left(\dfrac{Q_{^{16}O^{12}C^{18}O}}{Q_{^{16}O^{13}C^{18}O}}\right)$, as shown in Eqn. 10, each of which can be calculated using Eqn. 11.

For molecules with known zero point energies (obtained from ab initio and quantum mechanic molecular models), the partition function ratio is evaluated starting with the first vibration quantum number, rather than using $\dfrac{1}{2}\sum_i^{3n-5} \varpi_i$ to estimate the zero point energy. After this modification, the partition function ratio $\left(\dfrac{Q_{^{16}O^{13}C^{16}O}}{Q_{^{16}O^{12}C^{16}O}}\right)$ becomes:

$$\left(\frac{Q_{^{16}O^{13}C^{16}O}}{Q_{^{16}O^{12}C^{16}O}}\right)$$

$$= \frac{\sigma_{^{16}O^{12}C^{16}O}}{\sigma_{^{16}O^{13}C^{16}O}} e^{-(u_0^{^{16}O^{13}C^{16}O} - u_0^{^{16}O^{12}C^{16}O})} \prod_{i=1}^{3n-5} \frac{u_i^{^{16}O^{13}C^{16}O}}{u_i^{^{16}O^{12}C^{16}O}} \frac{1 - e^{-u_i^{^{16}O^{12}C^{16}O}}}{1 - e^{-u_i^{^{16}O^{13}C^{16}O}}} \tag{12}$$

where $u_0^{^{16}O^{13}C^{16}O} = \dfrac{hc\varpi_0^{^{16}O^{13}C^{16}O}}{kT}$, indicating the contribution from the zero point energy. We used Eqn. 11 and 12 to evaluate equilibrium constants of reactions involving multiply substituted isotopologues when approximating intramolecular bonds as harmonic oscillators. Eqn. 12 is better than Eqn. 11 in describing partition function ratios at low temperatures and was used whenever possible.

Because molecules both vibrate and rotate, centrifugal forces acting on intramolecular bonds make it difficult to separate vibrational and rotational contributions to the partition function and require that we treat these bonds as anharmonic. It is commonly assumed that this effect leads to insignificant corrections in calculated partition functions. However, it is conceivable that these terms could influence the stabilities of multiply substituted molecules, so we have evaluated them for all cases we deemed computationally tractable. For diatomic molecules, we use the anharmonic nonrigid rotor model (Pitzer, 1953; see Davidson, 1962, for a broader summary). In this model, the energy in each quantum level is described as a function of quantum numbers v and J:

$$\frac{\varepsilon_{v,J}}{hc} = \varpi_e\left(v + \frac{1}{2}\right) - \varpi_e x_e\left(v + \frac{1}{2}\right)^2 + B_e J(J + 1)$$
$$- DJ^2(J + 1)^2 - \alpha\left(v + \frac{1}{2}\right)J(J + 1) \quad (13)$$

where ϖ_e is the harmonic vibration wave number and is related to the second derivative of the potential curve at its minimum, $\varpi_e x_e$ describes the anharmonicity of the potential curve, x_e is the cubic anharmonic correction term and is half of the relative deviation of the harmonic vibration wave number (ϖ_e) from the first vibrational spacing (ϖ_0), which can be directly measured from infrared or Raman spectroscopic data; $B_e = \frac{h}{8\pi^2 I_e c}$ and is the rotational constant, where I_e is moment of inertia of the diatomic molecule, c is speed of light, and h is Plank's constant; J and v are the rotational and vibrational quantum numbers, respectively; $D = \frac{4B_e^3}{\varpi_e^3}$ and describes centrifugal stretching; and α is the vibration-rotation coupling constant.

After removing small, higher order terms and integrating v and J, the contribution of the rovibration partition function to the overall partition function can be separated into the product of three parts: (1) Q_0 is from the zero point energy contribution (Richet et al., 1977); (2) $Q_{harm-rigid}$, has the same meaning as in the harmonic oscillator and rigid motor models above; and (3) Q_{corr} is the deviation from the harmonic oscillator and rigid model due to anharmonicity. These terms can be shown to have the following form (Eqn. 8–40 in Davidson, 1962):

$$Q^{v-r} = Q_0 Q_{harm-rigid} Q_{corr} \quad (14)$$

$$Q_0 = e^{-\frac{\left(\frac{\varpi_e}{2} - \frac{\varpi_e x_e}{4}\right)hc}{kT}} \quad (15)$$

$$Q_{harm-rigid} = \frac{1}{\sigma y}\frac{1}{1 - e^{-u}} \quad (16)$$

$$Q_{corr} = 1 + \frac{2\gamma}{y} + \frac{\delta}{e^u - 1} + \frac{2xu}{(e^u - 1)^2} + \frac{y}{3} + \frac{y^2}{15} \quad (17)$$

where

$$u = \frac{hc(\varpi_e - 2\varpi_e x_e)}{kT}, \quad y = \frac{hc\left(B_e - \frac{\alpha}{2}\right)}{kT}, \quad \gamma = \frac{D}{B_e - \frac{\alpha}{2}}$$

and

$$\delta = \frac{\alpha}{B_e - \frac{\alpha}{2}}.$$

The full partition function Q_i including translational energy is:

$$Q_i = M_i Q_i^{v-r} \quad (18)$$

where M_i is the mass of isotopologue i. We used Eqn. 13 through 18 to evaluate equilibrium constants of reactions involving multiply substituted isotopologues when describing intramolecular bonds of diatomic molecules with an anharmonic model.

Anharmonic models of partition functions for polyatomic molecules are more complex than Eqn. 13 through 18 (e.g., Nielsen, 1951) and can only be approximated by numerically solving the Schrödinger equation using an accurate rovibrational potential energy surface, and considering the first several thousand rovibrational state energies. This would be unreasonably time-consuming for the relatively broad overview of isotopologues and temperatures we consider. However, we tested the validity of our simpler approximations by conducting a limited set of more accurate calculations of this type for CO, CO$_2$. The results, presented in the Appendix, are effectively indistinguishable from those produced using the Urey method at temperatures of less than 275 K. We suspect that differences between these methods at higher temperatures reflect limitations of the spectroscopic data for multiply substituted isotopologues at higher quantum states and do not reflect methodologic errors. We conclude that the harmonic oscillator approximation (Eqn. 11 and 12), in addition to being applicable to a large range of molecules and conditions, is sufficiently accurate for our purposes. We therefore focus on results of these simpler calculations in the following section.

3. APPLICATION TO COMMON MOLECULAR GASES

In this section, we use the algorithm developed in section 2 to calculate the equilibrium proportions of all stable isotopologues of N$_2$, O$_2$, NO, CO, CO$_2$, and N$_2$O between 1000 and 193 to 77 K based on published spectroscopic data. The lower temperature limit for each molecule is chosen to be its 1-atm boiling or, for CO$_2$, sublimation temperature (77.3 K for N$_2$, 81.6 for CO, 90.2 K for O$_2$, 121.3 for NO, 184.6 K for N$_2$O, and 192.6 for CO$_2$; Lide and Frederikse, 1994). This lower limit is somewhat arbitrary but focuses on the temperature ranges appropriate for most geochemical and cosmochemical problems of possible interest.

The input data and results of these calculations are organized below by molecular species, from the simplest (symmetric, diatomic molecules) to the most complex (N$_2$O). The precision and accuracy of our model calculations depend chiefly on the quality of the spectroscopic data, on the accuracy and completeness of the harmonic and anharmonic models of intramolecular bonds, and on the assumption of ideal mixing of all isotopologues of a given molecule. Before presenting our results, we first define terms that are useful for expressing the systematics of multiply substituted isotopologues.

3.1. Definition and Properties of Δ

To appreciate the magnitude of isotopic variations that could result from distinctive partition functions of multiply substituted isotopologues, it is useful to compare abundances of these species calculated as described in section 2 of this paper to those expected if all isotopes are randomly distributed among all isotopologues (the stochastic distribution). We define here the variable, Δ_i, to describe this difference:

$$\Delta_i = \left(\frac{R_{i-e}}{R_{i-r}} - 1\right) \times 1000 \quad (19)$$

where R_{i-e} is the abundance of an isotopologue of interest, i, divided by the abundance of the isotopologue having no rare

isotopes in the same pool of molecules, evaluated at thermodynamic equilibrium. For example, $R_{^{18}O^{13}C^{16}O-e} = \frac{\left[^{18}O^{13}C^{16}O\right]_e}{\left[^{16}O^{12}C^{16}O\right]_e}$. R_{i-r} is that same ratio in a pool of CO_2 molecules of the same bulk isotopic composition but having the stochastic distribution of isotopologues. R_{i-r} is a simple function of the abundances of isotopes contributing to a pool of isotopologues (e.g., $R_{^{18}O^{13}C^{16}O-r} = \frac{\left[^{18}O^{13}C^{16}O\right]_r}{\left[^{16}O^{12}C^{16}O\right]_r} = \frac{2\left[^{18}O\right]\left[^{13}C\right]\left[^{16}O\right]}{\left[^{12}C\right]\left[^{16}O\right]^2} = \frac{2\left[^{18}O\right]\left[^{13}C\right]}{\left[^{16}O\right]\left[^{12}C\right]}$). Values of Δ_i have units of per mill deviation from the stochastic distribution and are independent of bulk isotopic composition over the range of natural abundances of rare isotopes (because Δ_i values of singly substituted isotopologues are close to zero for these isotopic compositions, in which case Δ_i values of multiply substituted isotopologues only depend on K_i values). Positive and negative values of Δ_i correspond to enrichments and depletions, respectively, in the isotopologue, i, relative to the stochastic distribution.

3.2. Relationship Between Δ and K Values

An isotope exchange reaction only involving one doubly substituted isotopologue of a given molecule can be written as

$$A_1 + A_4 \overset{K}{\rightleftharpoons} A_2 + A_3 \qquad (20)$$

where A_4 is the doubly substituted isotopologue, A_1 is the isotopologue having no rare isotopes, and A_2 and A_3 are singly substituted isotopologues (note A_2 and A_3 can be the same isotopologue; e.g., reaction 8ii and 8vi). Based on the law of mass action and assuming ideal mixing of stable isotopes on a given molecular site, the following expressions can be used to describe the equilibrium constants for such reactions:

$$K = \frac{\left[A_2\right]\left[A_3\right]}{\left[A_1\right]\left[A_4\right]} \qquad (21)$$

$$K_r = \frac{\left[A_{2-r}\right]\left[A_{3-r}\right]}{\left[A_{1-r}\right]\left[A_{4-r}\right]} \qquad (22)$$

where K_r refers to the equilibrium constant for the stochastic (random) distribution. Also, from the definition of Δ_i in Eqn. 19 we know:

$$\frac{\left[A_i\right]}{\left[A_1\right]} = \left(\frac{\Delta_i}{1000} + 1\right) \cdot \frac{\left[A_{i-r}\right]}{\left[A_{1-r}\right]} \qquad (23)$$

After dividing Eqn. 21 by Eqn. 22 on both sides and replacing the concentration ratios with Δ values following Eqn. 23, we find:

$$\frac{K}{K_r} = \frac{\left(\frac{\Delta_2}{1000} + 1\right)\left(\frac{\Delta_3}{1000} + 1\right)}{\left(\frac{\Delta_1}{1000} + 1\right)\left(\frac{\Delta_4}{1000} + 1\right)} \qquad (24)$$

Taking the natural logarithm of both sides of Eqn. 24, and rearranging, we find the following expression for the Δ_4:

$$\ln\left(\frac{\Delta_4}{1000} + 1\right) = \ln\left(\frac{\Delta_2}{1000} + 1\right) + \ln\left(\frac{\Delta_3}{1000} + 1\right)$$
$$- \ln\left(\frac{\Delta_1}{1000} + 1\right) - \ln\frac{K}{K_r} \qquad (25)$$

Because we defined A_1 as the isotopologue having no rare isotopes, Δ_1, by definition, equals 0. When Δ_i is small (ca. <10‰), Eqn. 25 can be reduced to:

$$\Delta_4 \approx \Delta_2 + \Delta_3 - 1000\ln\frac{K}{K_r} \qquad (26)$$

based on the approximation that $ln(1 + x) \approx x$ when x is much smaller than 1.

For all populations of isotopologues of diatomic and symmetric triatomic molecules (i.e., CO_2, but not N_2O) having bulk isotopic compositions within the range typical of natural materials, Δ_i values of singly substituted isotopologues are near 0 (ca. <0.01‰) at temperatures of interest. In this case, the following simple relationship exists between value of K and value of Δ_4:

$$\Delta_4 \approx -1000\ln\frac{K}{K_r} \qquad (27)$$

Asymmetric triatomic molecules (among whose different isotopologues the highest symmetry is $C_{\infty v}$) such as N_2O are exceptions for which Δ_i values of singly substituted isotopologues can be far from 0 (see section 3.5). In the interests of completeness, we present both Δ_i values and K_i values for all isotope exchange reactions for each molecule considered in the following section. In general, these two sets of variables have simple relationships to one another, as in Eqn. 27. However, it is important to note that while the K values are independent of bulk composition, Δ_i values can differ significantly from the values we show for highly enriched bulk isotopic compositions.

3.3. Δ Values for Isotopic Masses

While it is possible to precisely measure abundances of doubly substituted isotopologues of some molecular gases, the instruments used for this purpose today do not have sufficient mass resolution to separate isotopologues that are isobars of one another. For example, measurements of $^{16}O^{13}C^{18}O$ presented by Eiler and Schauble (2004) must be corrected for minor contributions from $^{17}O^{12}C^{18}O$ and $^{17}O^{13}C^{17}O$ (much as conventional measurements of $\delta^{13}C$ must be corrected for contributions from the isobar, $^{16}O^{12}C^{17}O$; Santrock et al., 1985 and references therein). We report Δ_i values for all individual isotopologues in this paper both for completeness in our theoretical treatment and because it may be possible in the future to resolve some of these isobars. However, we also report Δ_i values calculated in the same fashion as defined in Eqn. 19, but including contributions from all isotopologues having a single nominal cardinal mass. For example, Δ_{47} for CO_2 is calculated as:
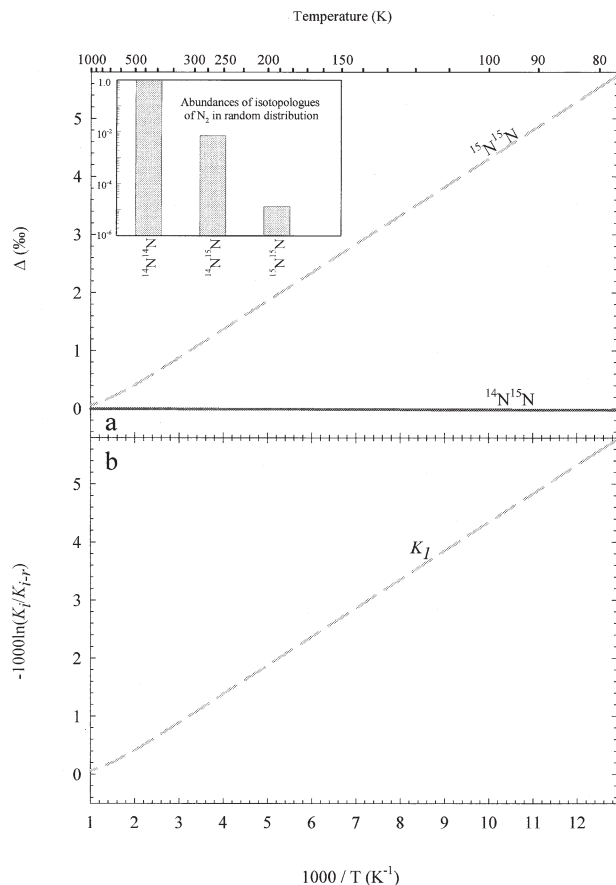
Fig. 2. (a) Variation of Δ values of all isotopologues of N_2 with 1/T; the inset shows the abundances of all isotopologues of N_2 for the stochastic distribution and an $^{15}N/^{14}N$ ratio equal to atmospheric N_2. (b) Variation of $-1000 \cdot \ln(K_i/K_{i-random})$ ($i = 1$) with 1000/T for the isotope exchange reaction in Eqn. 30.

$$\Delta_{47} = \left(\frac{\dfrac{[^{16}O^{13}C^{18}O] + [^{17}O^{12}C^{18}O] + [^{17}O^{13}C^{17}O]}{[^{16}O^{12}C^{16}O]}}{\dfrac{[^{16}O^{13}C^{18}O]_r + [^{17}O^{12}C^{18}O]_r + [^{17}O^{13}C^{17}O]_r}{[^{16}O^{12}C^{16}O]_r}} - 1 \right) \times 1000 \quad (28)$$

These Δ_i values calculated for a given cardinal mass obscure important details of the geochemistry of some isotopologues, but are useful because they provide a practical guide to the isotope effects that are measurable using existing technology.

3.4. Diatomic Molecules

Abundances of isotopologues of N_2, NO, CO, and O_2 were calculated using both the harmonic oscillator approximation (Eqn. 11 and 12) and the anharmonic model (Eqn. 13 through 17). Results of these calculations are presented in Figures 2 through 5 and in Table 2. We use molecular constants for $^{14}N^{14}N$, $^{14}N^{16}O$, $^{12}C^{16}O$, and $^{16}O_2$ taken from Huber and Herzberg (1979) (see Table 1). Properties of other isotopologues of these molecules were calculated based on spectro-
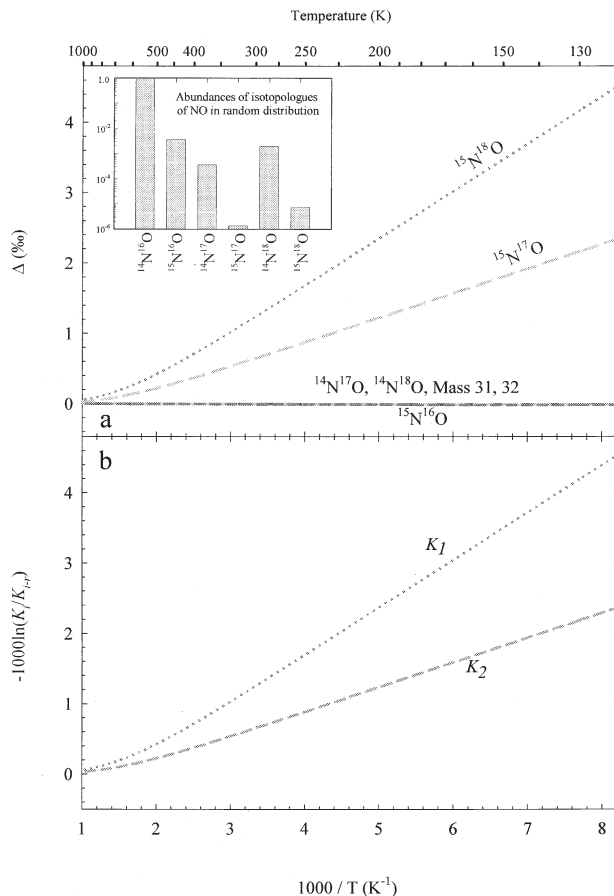
Fig. 3. (a) Variation of Δ values of all isotopologues of NO with 1/T; the inset shows the abundances of all isotopologues of NO for the stochastic distribution, an $^{15}N/^{14}N$ ratio equal to atmospheric N_2 and an oxygen isotope composition equal to VSMOW. (b) Variation of $-1000 \cdot \ln(K_i/K_{i-random})$ ($i = 1$ or 2) with 1000/T for the isotope exchange reactions in Eqn. 31i and 31ii.

scopic data and the following relationship from Dunham (1932):

$$\frac{\varpi_1}{\varpi_2} = \sqrt{\frac{\mu_2}{\mu_1}}; \frac{\varpi_1 x_{e1}}{\varpi_2 x_{e2}} = \frac{\mu_2}{\mu_1}; \frac{B_{e1}}{B_{e2}} = \frac{\mu_2}{\mu_1}; \frac{\alpha_{e1}}{\alpha_{e2}} = \left(\frac{\mu_2}{\mu_1}\right)^{3/2} \quad (29)$$

where $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ and is the reduced mass; ω_i, is the normal mode wave number (as above); x_e is the cubic anharmonic correction term; B_e is the rotational constant; α_e is vibration-rotation coupling constant; and subscripts 1 or 2 refer to different isotopologues of the same molecule. Isotopic masses and average natural abundances are from Walker et al. (1989).

3.4.1. N_2

The two required system components for N_2 were chosen to be $^{14}N^{14}N$ and $^{14}N^{15}N$. The independent exchange reaction that goes with these system components is:
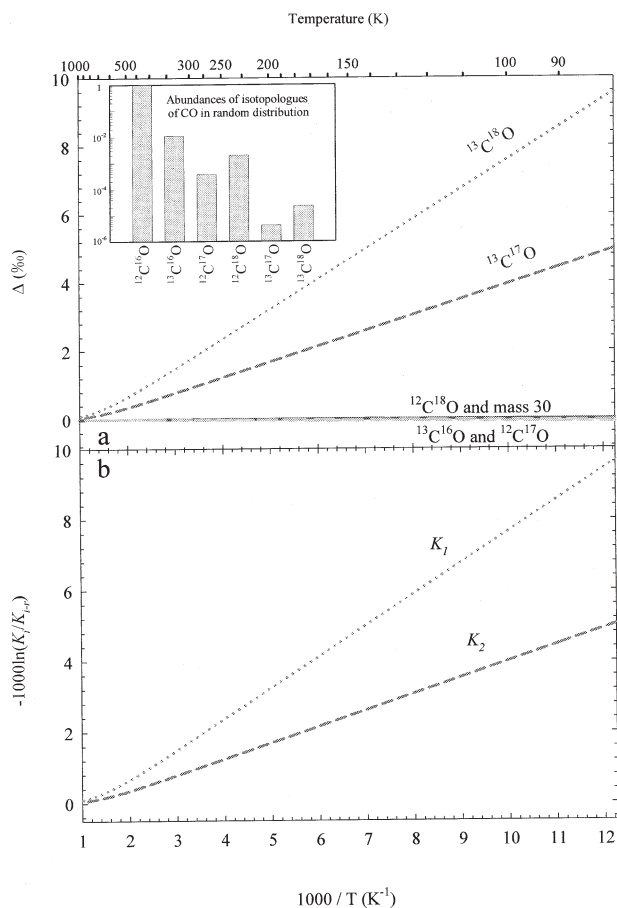
$$^{14}N^{14}N + {}^{15}N^{15}N \overset{K_1}{\rightleftharpoons} 2\,{}^{14}N^{15}N \quad (30)$$
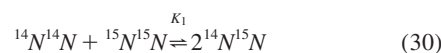
Fig. 4. (a) Variation of Δ values of all isotopologues of CO with 1/T; the inset shows the abundances of all isotopologues of CO for the stochastic distribution, a ^{13}C/^{12}C ratio equal to PDB, and an oxygen isotope composition equal to VSMOW. (b) Variation of $-1000 \cdot \ln(K_i/K_{i\text{-}random})$ ($i = 1$ or 2) with respect to 1000/T for the isotope exchange reactions in Eqn. 32i and 32ii.
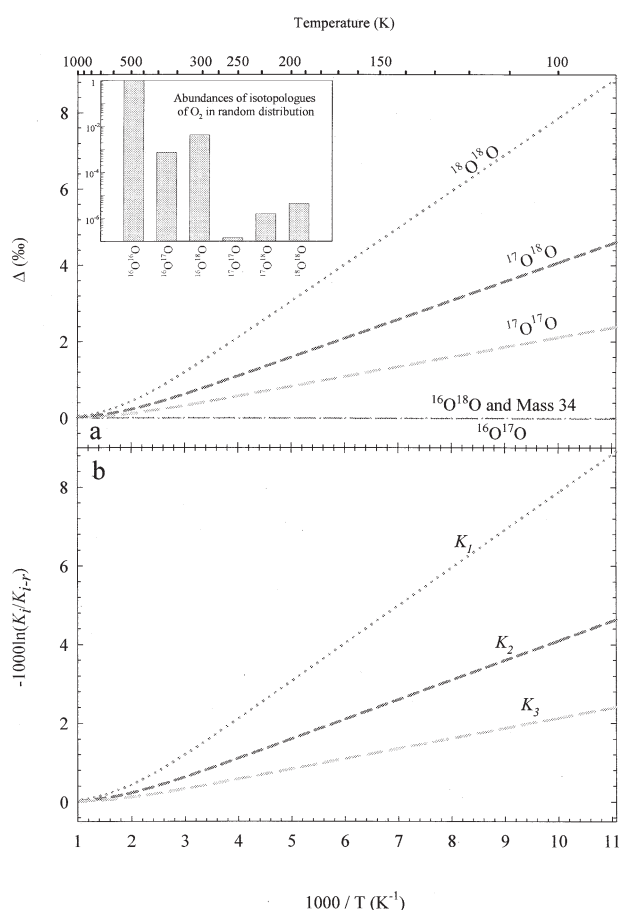
Fig. 5. (a) Variation of Δ values of all isotopologues of O$_2$ with 1/T; the inset shows the abundances of all isotopologues of O$_2$ for the stochastic distribution and an oxygen isotope composition equal to VSMOW. (b) Variation of $-1000 \cdot \ln(K_i/K_{i\text{-}random})$ ($i = 1$ to 3) with 1000/T for the isotope exchange reactions in Eqn. 33i through 33iii.

Results of our calculations for N$_2$ using the harmonic oscillator approximation are shown in Figure 2a and 2b and Table 2. Figure 2a shows Δ_i values of all isotopologues of N$_2$ as functions of 1/T; the inset shows the abundances of all isotopologues of N$_2$ for the stochastic distribution and a bulk isotopic composition equal to terrestrial atmospheric N$_2$ (IUPAC, 1994). Note that $\Delta_{^{14}N^{15}N}$ does not differ significantly from zero at any temperature within the range considered; i.e., this isotopologue is present in very nearly the abundance predicted for the stochastic distribution. In contrast, $\Delta_{^{15}N^{15}N}$ is ca. 1‰ at room temperature and increases with decreasing temperature. At temperatures less than ca. <400 K, $\Delta_{^{15}N^{15}N}$ varies linearly with 1/T. Figure 1b shows values of $-1000 \cdot \ln(K_i/K_{1\text{-}r})$ as a function of 1/T, where K_r is the equilibrium constant of reaction 30 ($K_{1\text{-}r} = 4$ for the stochastic distribution). The value of Δ_{30} exactly equals $\Delta_{^{15}N^{15}N}$.

If nitrogen in the earth's atmosphere were in equilibrium with respect to reaction 30, we would expect a ca. 1‰ excess of ^{15}N^{15}N beyond the stochastic distribution. This should be readily detectable using existing analytical methods, provided contributions from ^{14}N^{16}O and ^{12}C^{18}O (common products of fragmentation and oxidation reactions in mass spectrometer sources) can be minimized (it is unlikely they could be mass-resolved by a practical instrument). Given the slow rates of gas-phase isotope exchange reactions for most simple molecules, we think it likely that the earth's atmosphere is not in thermodynamic equilibrium, and instead that its ^{15}N^{15}N content reflects the net effects of fractionations accompanying various biologic and photochemical sources and sinks. Given the very long lifetime of N$_2$ in air, we think it possible that any such net enrichments or deficits could be large.

Table 1. Molecular constants for diatomic molecules of ^{16}O^{16}O ^{14}N^{14}N, ^{12}C^{16}O, and ^{14}N^{16}O; data are from Huber and Herzberg (1979). r_e is the equilibrium internuclear distance, other terms are defined in the text.

	ϖ_e (cm^{-1})	$\varpi_e x_e$ (cm^{-1})	B_e	α_e	r_e (Å)
^{14}N^{14}N	2358.570	14.324	1.63745	0.01791	1.21260
^{14}N^{16}O	1904.204	14.075	1.70493	0.01710	1.15077
^{12}C^{16}O	2169.814	13.288	1.93128	0.01750	1.12832
^{16}O^{16}O	1580.193	11.981	0.04747	0.01593	1.20752

Table 2. Calculated Δ for isotopologues of N_2, NO, CO, and O_2, at select temperature using harmonic or anharmonic oscillator models.

	200 K		300 K		1000 K	
	Harmonic	Anharmonic	Harmonic	Anharmonic	Harmonic	Anharmonic
N_2						
$^{14}N^{15}N$	−0.0069	−0.0069	−0.0039	−0.0039	−0.0002	−0.0002
$^{15}N^{15}N$	1.8619	1.8603	1.0456	1.0441	0.0636	0.0642
NO						
$^{15}N^{16}O$	−0.0053	−0.0053	−0.0028	−0.0028	−0.0001	−0.0001
$^{14}N^{17}O$	−0.0046	−0.0046	−0.0024	−0.0024	−0.0001	−0.0001
$^{15}N^{17}O$	1.2261	1.2240	0.6476	0.6458	0.0277	0.0281
$^{14}N^{18}O$	−0.0088	−0.0088	−0.0046	−0.0046	−0.0002	−0.0002
$^{15}N^{18}O$	2.3560	2.3518	1.2413	1.2378	0.0525	0.0533
CO						
$^{13}C^{16}O$	−0.0073	−0.0073	−0.0040	−0.0040	−0.0002	−0.0002
$^{12}C^{17}O$	−0.0189	−0.0188	−0.0104	−0.0103	−0.0005	−0.0005
$^{12}C^{18}O$	−0.0362	−0.0361	−0.0198	−0.0198	−0.0010	−0.0010
$^{13}C^{17}O$	1.6735	1.6714	0.9197	0.9179	0.0487	0.0487
$^{13}C^{18}O$	3.2134	3.2094	1.7623	1.7589	0.0924	0.0924
O_2						
$^{16}O^{17}O$	−0.0036	−0.0036	−0.0017	−0.0017	−0.0001	−0.0001
$^{16}O^{18}O$	−0.0069	−0.0068	−0.0033	−0.0033	−0.0001	−0.0001
$^{17}O^{17}O$	0.8274	0.8254	0.4063	0.4047	0.0128	0.0137
$^{17}O^{18}O$	1.5899	1.5862	0.7782	0.7751	0.0243	0.0261
$^{18}O^{18}O$	3.0569	3.0498	1.4910	1.4850	0.0460	0.0495

3.4.2. NO

The four required system components for NO were chosen to be $^{14}N^{16}O$, $^{15}N^{16}O$, $^{14}N^{17}O$, and $^{14}N^{18}O$. The two independent exchange reactions that go with these system components are:

$$^{14}N^{16}O + {}^{15}N^{17}O \overset{K_1}{\rightleftharpoons} {}^{15}N^{16}O + {}^{14}N^{17}O \qquad (31i)$$

$$^{14}N^{16}O + {}^{15}N^{18}O \overset{K_2}{\rightleftharpoons} {}^{15}N^{16}O + {}^{14}N^{18}O \qquad (31ii)$$
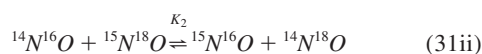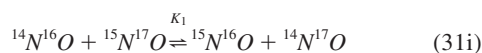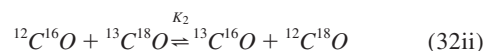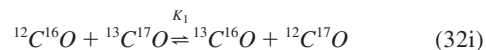
Results of our calculations for NO using the harmonic oscillator approximation are shown in Figure 3a and b and Table 2. Figure 3a shows the dependence of Δ values on $1/T$; the inset shows the abundances of all isotopologues for NO having the stochastic distribution, a bulk isotopic composition of N equal to atmospheric N_2 (IUPAC, 1994), and of O equal to Vienna Standard Mean Ocean Water (VSMOW) (IUPAC, 1994). Values of Δ_{15N18O} and Δ_{15N17O} are ∼1‰ at earth-surface temperatures, increase with decreasing temperature, and vary linearly with $1/T$ at temperatures less than 500 K. Figure 3b shows the dependences of $-1000 \cdot \ln(K_i/K_{i-r})$ ($i = 1$ or 2) on $1/T$ ($K_{i-r} = 1$ for both reactions). As for N_2, there is a simple relationship between Δ_i values and related K_i values (see section 3.2). The Δ_{32} value (a weighted sum of Δ_{15N17O} and Δ_{14N18O}) approximately equals 0 despite significant enrichments in $^{15}N^{17}O$ because the abundance ratio, $\dfrac{\left[^{15}N^{17}O\right]}{\left[^{14}N^{18}O\right]}$, is very small; Δ_{33} exactly equals Δ_{15N18O}.

The atmospheric budget of NO is influenced by emissions from soils (particularly fertilized agricultural fields) and a complex set of photochemical sources and sinks (including transfer between NO and NO_2). The budget has not been well studied by conventional stable isotope techniques, perhaps because of the low mixing ratio of nitric oxide in air (tens of pptv). We can think of no basis for confidently predicting the abundances of

$^{15}N^{17}O$ and $^{15}N^{18}O$ in air, although it seems reasonable to suspect they could be sensitive to the balance between soil sources vs. atmospheric photochemical sources and sinks.

3.4.3. CO

The four required system components for CO were chosen to be $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{17}O$, and $^{12}C^{18}O$. The two independent exchange reactions that go with these system components are:

$$^{12}C^{16}O + {}^{13}C^{17}O \overset{K_1}{\rightleftharpoons} {}^{13}C^{16}O + {}^{12}C^{17}O \qquad (32i)$$

$$^{12}C^{16}O + {}^{13}C^{18}O \overset{K_2}{\rightleftharpoons} {}^{13}C^{16}O + {}^{12}C^{18}O \qquad (32ii)$$
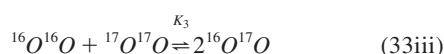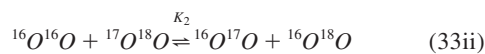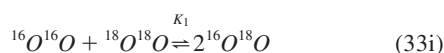
Results of our calculations for CO using the harmonic oscillator approximation are shown in Figure 4a and b and Table 2. Figure 4a shows the dependence of Δ values on $1/T$; the inset shows the abundances of all isotopologues for CO having the stochastic distribution, a $^{13}C/^{12}C$ ratio equal to Pee Dee Belemnite (PDB) (Craig, 1957), and an oxygen isotope composition equal to VSMOW (IUPAC, 1994). Values of Δ_{13C18O} and Δ_{13C17O} are ∼1‰ at earth-surface temperatures, increase with decreasing temperature, and vary linearly with $1/T$ at temperatures <600 K. Figure 4b shows the dependence of $-1000 \cdot \ln(K_i/K_{i-r})$ ($i = 1$ or 2) on $1/T$ ($K_{i-r} = 1$ for both reactions). The Δ_{30} value (equal to the weighted sum of Δ_{12C18O} and Δ_{13C17O}) approximately equals 0 because the abundance ratio, $\dfrac{\left[^{13}C^{17}O\right]}{\left[^{12}C^{18}O\right]}$, is very small; Δ_{31} exactly equals Δ_{13C18O}.

The natural atmospheric budget of CO includes sources from fossil fuel and biomass combustion and photo-oxidation of volatile hydrocarbons, and sinks to soil uptake and oxidation by atmospheric radicals. It is difficult to predict the expected impact of these processes on abundances of multiply substituted isotopologues, although experience with CO_2 (discussed

below) suggests combustion sources will be near the stochastic distribution. Losses to soil are suspected to rate limited by soil diffusion and may involve fractionations controlled by the kinetic theory of gases (see Eiler and Shauble (2004) for examples of such fractionations of $^{18}O^{13}C^{16}O$). Photochemical sources and sinks are less easily predicted and suggest we must await experimental study.

3.4.4. O_2

The three required independent system components for O_2 are chosen to be $^{16}O^{16}O$, $^{16}O^{17}O$, and $^{16}O^{18}O$. The set of three independent reactions that go with these system components is:

$$^{16}O^{16}O + {}^{18}O^{18}O \overset{K_1}{\rightleftharpoons} 2\,^{16}O^{18}O \tag{33i}$$

$$^{16}O^{16}O + {}^{17}O^{18}O \overset{K_2}{\rightleftharpoons} {}^{16}O^{17}O + {}^{16}O^{18}O \tag{33ii}$$

$$^{16}O^{16}O + {}^{17}O^{17}O \overset{K_3}{\rightleftharpoons} 2\,^{16}O^{17}O \tag{33iii}$$

Results of our calculations for O_2 using the harmonic oscillator approximation are shown in Figure 5a and b and Table 2. Figure 5a shows Δ values of all isotopologues of O_2 as functions of 1/T; the inset shows the abundances of all isotopologues for O_2 having the stochastic distribution and an oxygen isotope composition equal to VSMOW (IUPAC, 1994). Values of $\Delta_{17_O17_O}$, $\Delta_{17_O18_O}$, and $\Delta_{18_O18_O}$ are ca. 1‰ at earth-surface temperatures, increase with decreasing temperature, and vary linearly with 1/T at temperatures less than ca. 400 K. Figure 5b shows values of $-1000 \cdot \ln(K_i/K_{i-r})$ (i = 1, 2 and 3) as functions of 1/T. The value of Δ_{34} (equal to the weighted sum of $\Delta_{16_O18_O}$ and $\Delta_{17_O17_O}$) approximately equals 0 because the abundance ratio, $\dfrac{\left[^{17}O^{17}O\right]}{\left[^{16}O^{18}O\right]}$, is very small; Δ_{35} exactly equals $\Delta_{17_O18_O}$ and Δ_{36} exactly equals $\Delta_{18_O18_O}$.

The atmospheric budget of O_2 is dominated by photosynthetic sources and respiration sinks, resulting in a distinctive heavy-isotope enrichment referred to as the Dole effect (Dole, 1935), which has been ascribed to fractionations during respiration (Lane and Dole, 1956). In the absence of other fractionations, the kinetic theory of gases predicts this should lead to several tenths of per mill depletions of $\Delta_{17_O18_O}$ and $\Delta_{18_O18_O}$ rather than values of ca. +1‰ predicted for thermodynamic equilibrium. However, the Dole effect is also influenced by stratospheric ozone chemistry and by fossil fuel and biomass combustion. In particular, atmospheric O_2 is anomalously low in $\delta^{17}O$ given its $\delta^{18}O$ value (i.e., it lies below the terrestrial fractionation line defined by earth rocks and waters on a plot of $\delta^{17}O$ vs. $\delta^{18}O$; Luz et al., 1999). This phenomenon has been ascribed to nonmass-dependent isotopic fractionations associated with ozone chemistry (Luz et al., 1999) or to unusual mass dependence of diffusive fractionations during respiration (Young et al., 2002). While the fractionation of $^{18}O^{18}O$ and $^{17}O^{18}O$ during natural ozone chemistry are not well known, we speculate that they could differ from those predicted for thermodynamic equilibrium and diffusive fractionation, and therefore might constrain contributions of these various processes to the overall atmospheric budget.

Results of calculations for N_2, NO, CO, and O_2 using an anharmonic model of intramolecular bonds and temperatures of 200 K, 300 K, and 1000 K are listed in Table 2, where they can be compared with results using the harmonic oscillator approximation. Note that Δ values calculated using the harmonic oscillator model are slightly larger at low temperatures (ca. 200 K) and slightly lower at high temperatures (ca. 1000 K) than those calculated using the anharmonic nonrigid rotor model; thus, results plotted in Figures 2 through 5 contain small systematic errors reflecting imperfections in the harmonic oscillator model. However, these errors are a small fraction of Δ values at any given temperature, and we conclude that the harmonic oscillator model is sufficiently accurate for the purposes of interpreting measured abundances of multiply substituted isotopologues.

Note that all values of Δ for the diatomic molecules discussed above vary linearly with 1/T when temperature is lower than ca. 600 to 400 K. This reflects the same factors that control the temperature dependence of better-known intermolecular isotope exchange reactions (e.g., Bigeleisen and Mayer, 1947; O'Neil, 1986). Bigeleisen and Mayer (1947) showed that expressions for partition function ratios such as Eqn. 11 can be approximated as follows:

$$\frac{Q_2}{Q_1} = 1 + \left(\frac{1}{2} - \frac{1}{U_2} + \frac{1}{e^{-U_2}-1}\right)(U_1 - U_2) = 1 + G(U_1 - U_2) \tag{34}$$

where $U_i = hc\omega_i/kT$. Because vibrational wave numbers for the molecules considered in this section are generally between 1600 to 2400 cm^{-1}, U_2 values are generally larger than 5 when temperature is below 400 K. In this case, G approaches a value of 0.5 and partition function ratios vary linearly with 1/T. At higher temperatures, where U_2 values are smaller than 5, G converges toward a value of $U_2/12$ and partition function ratios instead vary linearly with 1/T^2. Hence, equilibrium constants for the isotope exchange reactions we consider should vary linearly with 1/T below ca. 600 to 400 K, and nonlinearly with 1/T at higher temperatures.

3.5. Triatomic Molecules

As the number of atoms in a molecule increases, it becomes increasingly difficult to predict equilibrium distribution of isotopologues of the molecule, both due to gaps in the spectroscopic data and the larger number of independent isotope exchange reactions that must be considered. Moreover, anharmonic models of intramolecular bonds are more difficult to formulate and evaluate, because the vibrational-rotational potential energy surface is complicated and the interaction between rotation and vibration is often strong. For these reasons, the only triatomic (or higher order) molecules we consider are CO_2 and N_2O, both of which have full spectroscopic data and accurate potential energy surfaces available in the literature (Chedin, 1979; Chedin and Teffo, 1984; Zúñiga et al., 1999; Zúñiga et al., 2001). The models we present for these molecules are based upon the same "Urey-type" treatment of vibrational energies discussed above. The Appendix presents additional calculations made using higher-order theory to test the validity of the approximations used in this approach. These tests sug-

Table 3. Calculated zero point energies and normal mode wave numbers for all isotopologues of CO_2 and N_2O, using potential energy surfaces from Zuniga et al. (2001) and Zuniga et al. (1999).

	Zero point energy(cm^{-1})	ϖ_1(cm^{-1})	$\varpi_2^{\dagger}$(cm^{-1})	ϖ_3(cm^{-1})
CO_2				
$^{16}O^{12}C^{16}O$	2525.394	1348.479	670.315	2387.185
$^{16}O^{13}C^{16}O$	2472.905	1348.479	651.237	2319.243
$^{16}O^{12}C^{17}O$	2507.955	1328.175	667.609	2377.682
$^{16}O^{12}C^{18}O$	2492.277	1309.544	665.205	2369.462
$^{16}O^{13}C^{17}O$	2455.240	1328.154	648.452	2309.472
$^{17}O^{12}C^{17}O$	2490.437	1308.042	664.892	2367.872
$^{16}O^{13}C^{18}O$	2439.355	1309.467	645.976	2301.041
$^{17}O^{12}C^{18}O$	2474.686	1289.553	662.478	2359.382
$^{17}O^{13}C^{17}O$	2437.498	1308.042	645.654	2299.360
$^{18}O^{12}C^{18}O$	2458.866	1271.185	660.056	2350.649
$^{17}O^{13}C^{18}O$	2421.542	1289.536	643.168	2290.624
$^{18}O^{13}C^{18}O$	2405.519	1271.185	640.673	2281.620
N_2O				
$^{14}N^{14}N^{16}O$	2362.891	1293.360	594.047	2273.531
$^{14}N^{15}N^{16}O$	2324.403	1291.559	580.468	2224.518
$^{15}N^{14}N^{16}O$	2339.811	1276.422	590.511	2250.898
$^{15}N^{15}N^{16}O$	2301.072	1275.062	576.848	2201.112
$^{14}N^{14}N^{17}O$	2347.536	1270.870	591.559	2269.847
$^{14}N^{15}N^{17}O$	2308.882	1268.802	577.922	2220.888
$^{15}N^{14}N^{17}O$	2324.378	1254.108	588.008	2246.910
$^{15}N^{15}N^{17}O$	2285.474	1252.506	574.286	2197.158
$^{14}N^{14}N^{18}O$	2333.729	1250.451	589.349	2266.682
$^{14}N^{15}N^{18}O$	2294.920	1248.131	575.659	2217.776
$^{15}N^{14}N^{18}O$	2310.497	1233.829	585.785	2243.483
$^{15}N^{15}N^{18}O$	2271.441	1231.997	572.009	2193.768

† $\varpi_2 =$ is doubly degenerate.

gest the "Urey" method of calculating partition function ratios is adequate for our purposes, even for triatomic molecules.
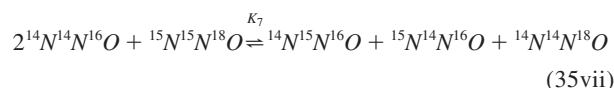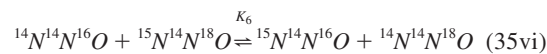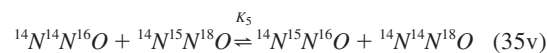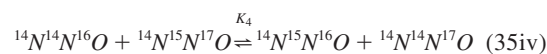
3.5.1. CO_2

The four required system components for CO_2 were chosen to be $^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$, $^{16}O^{12}C^{17}O$, and $^{16}O^{12}C^{18}O$. The set of eight independent exchange reactions that go with these system components are listed above in Eqn. 8i through 8viii (section 2.1). Zero point energy and normal mode frequencies of CO_2 isotopologues (Table 3) were calculated using the potential energy surface from Zúñiga et al. (2001). Results of our calculations for CO_2 using the harmonic oscillator approximation are shown in Figure 6a and b and Table 4. Figure 6a shows Δ values of all isotopologues of CO_2 as functions of 1/T; the inset shows the abundances of all isotopologues for CO_2 having the stochastic distribution, a $^{13}C/^{12}C$ ratio equal to PDB (Craig, 1957) and an oxygen isotope composition equal to VSMOW (IUPAC, 1994). Values of $\Delta_{^{18}O^{13}C^{18}O}$, $\Delta_{^{17}O^{13}C^{18}O}$, $\Delta_{^{17}O^{13}C^{17}O}$, $\Delta_{^{16}O^{13}C^{18}O}$, $\Delta_{^{16}O^{13}C^{17}O}$ and $\Delta_{^{18}O^{12}C^{18}O}$ are all between ca. 0.5‰ and 2‰ at earth-surface temperatures, increase with decreasing temperature, and vary linearly with 1/T at temperatures <400 K. Figure 6b shows values of $-1000 \cdot \ln(K_i/K_{i-r})$ ($i = 1$ through 8) as functions of 1/T (values of K_{i-r} for these reactions are listed in section 2 immediately following Eqn. 9. The Δ_{46} value (equal to the weighted sum of $\Delta_{^{16}O^{12}C^{18}O}$, $\Delta_{^{17}O^{12}C^{17}O}$ and $\Delta_{^{16}O^{13}C^{17}O}$) is ~0 due to low abundances of $^{17}O^{12}C^{17}O$ and $^{16}O^{13}C^{17}O$ compared with that of $^{16}O^{12}C^{18}O$ (Fig. 5a). Similarly, Δ_{47} (equal to the weighted sum

of $\Delta_{^{16}O^{13}C^{18}O}$, $\Delta_{^{17}O^{12}C^{18}O}$ and $\Delta_{^{17}O^{13}C^{17}O}$) is only slightly greater than $\Delta_{^{16}O^{13}C^{18}O}$, and Δ_{48} (equal to the weighted sum of $\Delta_{^{17}O^{12}C^{18}O}$ and $\Delta_{^{17}O^{13}C^{18}O}$) is only slightly greater than $\Delta_{^{18}O^{12}C^{18}O}$ at any given temperature. Alternate calculated abundances of CO_2 isotopologues using spectroscopic data from Chedin (1979) and Chedin and Teffo (1984) are also provided in Table 4 for comparison. Differences between these results and those based on the Zúñiga et al. (2001) potential energy surface model are up to $\sim$ 0.3‰ at 200 K (though generally <0.1‰). These differences are detectable with existing analytical methods (Eiler and Schauble, 2004) and suggest that analyses of Δ_i values in equilibrated mixtures of CO_2 isotopologues could be used to chose between, or otherwise constrain, models of the CO_2 molecule.

To the best of our knowledge, $^{18}O^{13}C^{16}O$ is the only multiply substituted isotopologue to be precisely measured in atmospheric samples. These data are presented in Eiler and Schauble (2004). Briefly, the atmosphere is enriched by ca. 0.7 to 0.8‰ in Δ_{47}, consistent with thermodynamic equilibrium at earth-surface temperatures being the first-order control, but with a small ($\sim$0.2‰) but consistent deficit in Δ_{47} that might reflect diffusive fractionations during photosynthetic carbon fixation, and additions to air of high-temperature anthropogenic CO_2. Variations in Δ_{47} with time and location are likely to result from variable temperatures of equilibration between air and seawater or plant leaf water and variable contributions of anthropogenic sources. It is possible that the abundances of multiply substituted isotopologues of CO_2 in the stratosphere, where photochemical reactions contribute significantly to its budget, will differ even more greatly from the existing tropospheric measurements.

3.5.2. N_2O

The four required system components for N_2O were chosen to be $^{14}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, $^{14}N^{14}N^{17}O$, and $^{14}N^{14}N^{18}O$. The set of eight independent exchange reactions that go with these system components are:

$$^{14}N^{14}N^{16}O + {}^{15}N^{15}N^{16}O \overset{K_1}{\rightleftharpoons} {}^{14}N^{15}N^{16}O + {}^{15}N^{14}N^{16}O \quad (35i)$$

$$^{14}N^{14}N^{16}O + {}^{15}N^{14}N^{17}O \overset{K_2}{\rightleftharpoons} {}^{15}N^{14}N^{16}O + {}^{14}N^{14}N^{17}O \quad (35ii)$$

$$2{}^{14}N^{14}N^{16}O + {}^{15}N^{15}N^{17}O \overset{K_3}{\rightleftharpoons} {}^{14}N^{15}N^{16}O + {}^{15}N^{14}N^{16}O + {}^{14}N^{14}N^{17}O$$
$$(35iii)$$

$$^{14}N^{14}N^{16}O + {}^{14}N^{15}N^{17}O \overset{K_4}{\rightleftharpoons} {}^{14}N^{15}N^{16}O + {}^{14}N^{14}N^{17}O \quad (35iv)$$

$$^{14}N^{14}N^{16}O + {}^{14}N^{15}N^{18}O \overset{K_5}{\rightleftharpoons} {}^{14}N^{15}N^{16}O + {}^{14}N^{14}N^{18}O \quad (35v)$$

$$^{14}N^{14}N^{16}O + {}^{15}N^{14}N^{18}O \overset{K_6}{\rightleftharpoons} {}^{15}N^{14}N^{16}O + {}^{14}N^{14}N^{18}O \quad (35vi)$$

$$2{}^{14}N^{14}N^{16}O + {}^{15}N^{15}N^{18}O \overset{K_7}{\rightleftharpoons} {}^{14}N^{15}N^{16}O + {}^{15}N^{14}N^{16}O + {}^{14}N^{14}N^{18}O$$
$$(35vii)$$

$$^{14}N^{15}N^{16}O \overset{K_8}{\rightleftharpoons} {}^{15}N^{14}N^{16}O \quad (35viii)$$
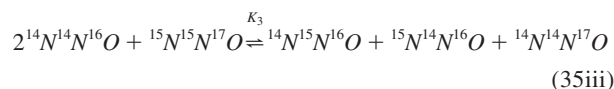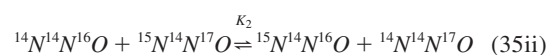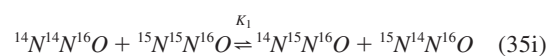
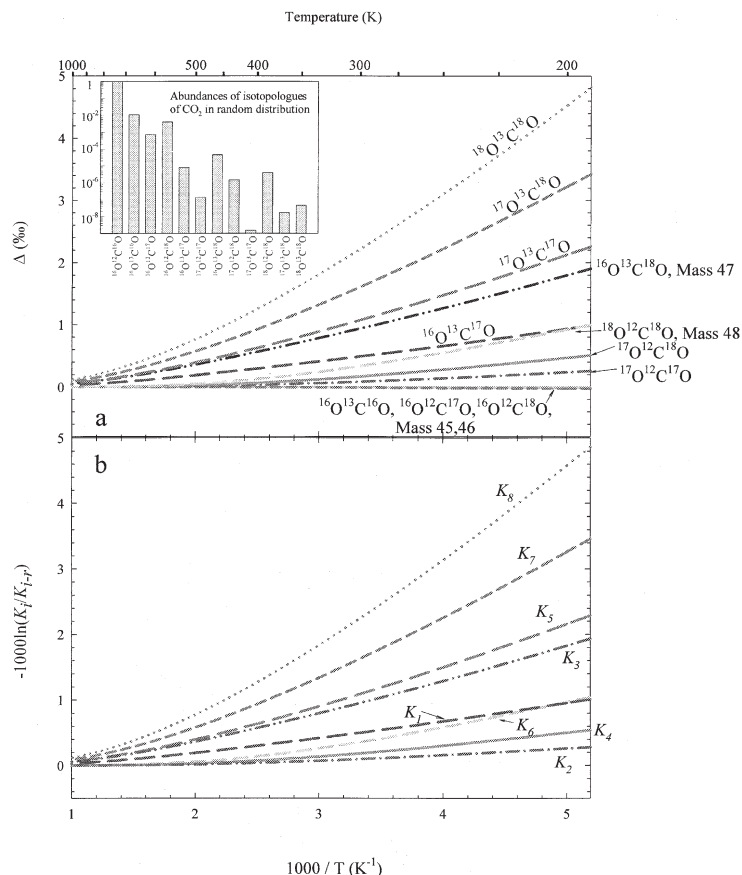Zero point energies and normal mode frequencies for N_2O

Fig. 6. (a) Variation of Δ values of all isotopologues of CO_2 with 1/T; the inset shows the abundances of all isotopologues of CO_2 for the stochastic distribution, a $^{13}C/^{12}C$ ratio equal to PDB, and an oxygen isotope composition equal to VSMOW. (b) Variation of $-1000 \cdot \ln(K_i/K_{i\text{-}random})$ ($i = 1$ to 8) with 1000/T for the isotope exchange reactions in Eqn. 8i through 8viii.

(Table 3) were calculated using the potential energy surface of Zúñiga et al. (1999). Results of our calculations for N_2O using the harmonic oscillator approximation are shown in Figure 7a through c, Figure 8a and b and Table 4. Figure 7a through c shows Δ values of all isotopologues of N_2O as functions of 1/T; the inset to Figure 7a shows abundances of all isotopologues for N_2O having the stochastic distribution, a $^{15}N/^{14}N$ ratio equal to atmospheric N_2 (IUPAC, 1994), and an oxygen isotope composition equal to VSMOW (IUPAC, 1994). Figure 8a and b shows values of $-1000 \cdot \ln(K_i/K_{i\text{-}r})$ ($i = 1$ through 8) as functions of 1/T. Note that, unlike all other molecules considered in this study, relationships between $-1000 \cdot \ln(K_i/K_{i\text{-}r})$ and Δ_i values are not simple for N_2O. Values of $-1000 \cdot \ln(K_i/K_{i\text{-}r})$ for reactions 35i through 35vii have magnitudes and temperature dependences resembling those of analogous reactions of other molecules considered in this study, whereas $-1000 \cdot \ln(K_i/K_{i\text{-}r})$ for reaction 35viii is exceptionally large and strongly dependent on temperature. The aberrant behaviors of N_2O isotopologues (discussed below) can be attributed to this large equilibrium constant for reaction 35viii.

There are several noteworthy differences between results for N_2O and CO_2 despite similarities in masses of isotopologues and their constituent atoms. First, values of $\Delta_{^{15}N^{15}N^xO}$ (where $x =$ 16, 17, or 18) differ significantly from zero at low temperature, but do not increase monotonically with decreasing temperature.

Second, values of $\Delta_{^{14}N^{15}N^xO}$ are large positive numbers, more than an order of magnitude larger than Δ values for any CO_2 isotopologue. Finally, values of $\Delta_{^{15}N^{14}N^xO}$ are large negative numbers, also more than an order of magnitude larger in absolute value than Δ values for any CO_2 isotopologue, and the only Δ values of any isotopologue considered in this study that are significantly less than 0. Note that large positive and negative Δ values for the $^{14}N^{15}N^{18}O$ and $^{15}N^{14}N^{18}O$ isotopologues are similar in absolute value to one another at any given temperature, so that Δ_{47} (equal to the weighted sum of $\Delta_{^{14}N^{15}N^{18}O}$, $\Delta_{^{15}N^{14}N^{18}O}$, and $\Delta_{^{15}N^{15}N^{17}O}$) is only ca. 0.5‰ at earth-surface temperatures and has a temperature dependence resembling doubly substituted isotopologues of other molecules we considered.

The unusual behaviors of N_2O result from the affinity of ^{15}N for the central position in N_2O, stabilizing $^{14}N^{15}N^xO$ species relative to $^{15}N^{14}N^xO$ species. The zero-point energies of $^{14}N^{15}N^xO$ species are ca. 15.5 cm^{-1} less than those of $^{15}N^{14}N^xO$ species having the same mass (Table 3). These differences lead to ca. 80‰ enrichment of $^{14}N^{15}N^{16}O$ relative to $^{15}N^{14}N^{16}O$ at 200 K. Furthermore, the complex temperature dependence of $\Delta_{^{15}N^{15}N^{16}O}$ can be explained by different temperature dependencies of the reduced partition functions of $\Delta_{^{14}N^{15}N^{16}O}$ and $\Delta_{^{15}N^{14}N^{16}O}$. Similar to Eqn. 25, the relationship between $\Delta_{^{15}N^{15}N^{16}O}$ and K_1 is:

Table 4. Comparison of calculated Δ values for isotopologues of N_2O and CO_2 at select temperatures, using data in Table 3 (I) and data from Zuniga et al. (2001) for CO_2 and Zuniga et al. (2003) for N_2O (II).

	200 K		300 K		1000 K	
	I	II	I	II	I	II
CO_2						
$^{16}O^{13}C^{16}O$	−0.0082	−0.0082	−0.0043	−0.0043	−0.0003	−0.0003
$^{16}O^{12}C^{17}O$	−0.0117	−0.0121	−0.0060	−0.0062	−0.0003	−0.0004
Mass 45	−0.0084	−0.0085	−0.0044	−0.0044	−0.0003	−0.0003
$^{16}O^{12}C^{18}O$	−0.0225	−0.0228	−0.0114	−0.0116	−0.0007	−0.0007
$^{16}O^{13}C^{17}O$	0.9347	0.9477	0.4888	0.4982	0.0306	0.0327
$^{17}O^{12}C^{17}O$	0.2370	0.4537	0.0848	0.2124	−0.0007	0.0181
Mass 46	−0.0205	−0.0208	−0.0104	−0.0106	−0.0006	−0.0006
$^{16}O^{13}C^{18}O$	1.7977	1.8093	0.9384	0.9482	0.0582	0.0609
$^{17}O^{12}C^{18}O$	0.4674	0.5187	0.1681	0.2011	−0.0010	0.0056
$^{17}O^{13}C^{17}O$	2.1273	2.3922	1.0738	1.2332	0.0616	0.0865
Mass 47	1.7552	1.7680	0.9138	0.9243	0.0563	0.0592
$^{18}O^{12}C^{18}O$	0.9217	1.0100	0.3329	0.3900	−0.0013	0.0104
$^{17}O^{13}C^{18}O$	3.2220	3.5192	1.6078	1.7888	0.0892	0.1187
Mass 48	0.9311	1.0202	0.3381	0.3956	−0.0010	0.0108
$^{18}O^{13}C^{18}O$	4.5322	4.6997	2.2192	2.3296	0.1169	0.1391
N_2O						
$^{14}N^{15}N^{16}O$	39.3299	39.3517	22.8067	22.8072	3.6144	3.6031
$^{15}N^{14}N^{16}O$	−39.3302	−39.3736	−22.8089	−22.8282	−3.6146	−3.6116
$^{14}N^{14}N^{17}O$	−0.0032	−0.0030	−0.0015	−0.0013	−0.0001	0.0000
Mass 45	−0.0003	−0.0106	−0.0011	−0.0101	−0.0001	−0.0041
$^{15}N^{15}N^{16}O$	−0.4564	2.4191	0.0727	2.5882	0.0261	1.1336
$^{14}N^{15}N^{17}O$	39.9751	39.9314	23.1163	23.0706	3.6293	3.6018
$^{15}N^{14}N^{17}O$	−39.1061	−39.1274	−22.7294	−22.7313	−3.6155	−3.6056
$^{14}N^{14}N^{18}O$	−0.0062	−0.0065	−0.0028	−0.0030	−0.0001	−0.0002
Mass 46	−0.0086	0.0103	−0.0020	0.0146	0.0001	0.0074
$^{15}N^{15}N^{17}O$	0.3899	0.3162	0.4538	0.3991	0.0401	0.0197
$^{14}N^{15}N^{18}O$	40.5659	40.5792	23.3982	23.3915	3.6426	3.6272
$^{15}N^{14}N^{18}O$	−38.8990	−38.8564	−22.6568	−22.6107	−3.6163	−3.5874
Mass 47	0.8333	0.8612	0.3708	0.3904	0.0131	0.0199
$^{15}N^{15}N^{18}O$	1.1670	1.1484	0.8012	0.7867	0.0527	0.0454

$$\ln\left(\frac{\Delta_{15N15N16O}}{1000} + 1\right) = \ln\left(\frac{\Delta_{15N14N16O}}{1000} + 1\right)$$

$$+ \ln\left(\frac{\Delta_{14N15N16O}}{1000} + 1\right) - \ln\frac{K_1}{K_{1-r}} \quad (36)$$

At low temperatures (e.g., <250 K), $\ln\left(\frac{\Delta_{15N14N16O}}{1000} + 1\right) + \ln$ $\left(\frac{\Delta_{14N15N16O}}{1000} + 1\right)$ is a negative number and smaller than $\ln\frac{K_1}{K_{1-r}}$, giving rise to the negative $\Delta_{15N15N16O}$ value; while at high temperatures, it is a small negative number close to zero.

Alternative calculations of the abundances of N_2O isotopologues using spectroscopic data, zero point energies, and normal mode frequencies from Zúñiga et al. (2003) are also listed in Table 4 for comparison. These results are generally similar to those based on the Zúñiga et al. (1999) potential energy surface, although a notable exception is the ca. 2.5‰ difference in $\Delta_{15N15N16O}$ at low temperature. This difference is difficult to understand given agreement for all other isotopologues; one possible explanation is that the spectroscopic data for $^{15}N^{15}N^{16}O$ from Zúñiga et al. (2003) are not consistent with those for other isotopologues considered in that study.

The atmospheric budget of N_2O is dominated by sources from the terrestrial biosphere and oceans and photochemical sinks (Rahn and Wahlen, 2000; Toyoda et al., 2001; McLinden

et al., 2003). Recent research on its budget has been motivated, in part, by the fact that it is a greenhouse gas with a large, though indirect, anthropogenic source (resulting from use of agricultural fertilizers). Stable isotope data are a prominent part of this research and take advantage of large isotopic contrasts between biosphere sources and the mean atmosphere. The large distinctive thermodynamic fractionations predicted for N_2O isotopologues (Figs. 7 and 8), combined with strong isotopic fractionations associated with photolysis (Blake et al., 2003), suggest that measurements of multiply substituted isotopologues could contribute additional constraints to this problem.

4. DISCUSSION AND CONCLUSIONS

Results of our calculations can be summarized as follows.

1. Where as most singly substituted isotopologues do not have measurable deviations from the stochastic distribution, multiply substituted isotopologues typically have per mill level enrichments at earth-surface temperatures.
2. In most cases, deviations from the stochastic distribution (Δ values) increase linearly with 1/T at temperatures <ca. 600 to 400 K.
3. Abundances of multiply substituted isotopologues of N_2O are exceptions to the preceding generalizations. They vary complexly with temperature and include tens of per mill enrichments and depletions of $^{14}N^{15}N^xO$, and $^{15}N^{14}N^xO$, respec-
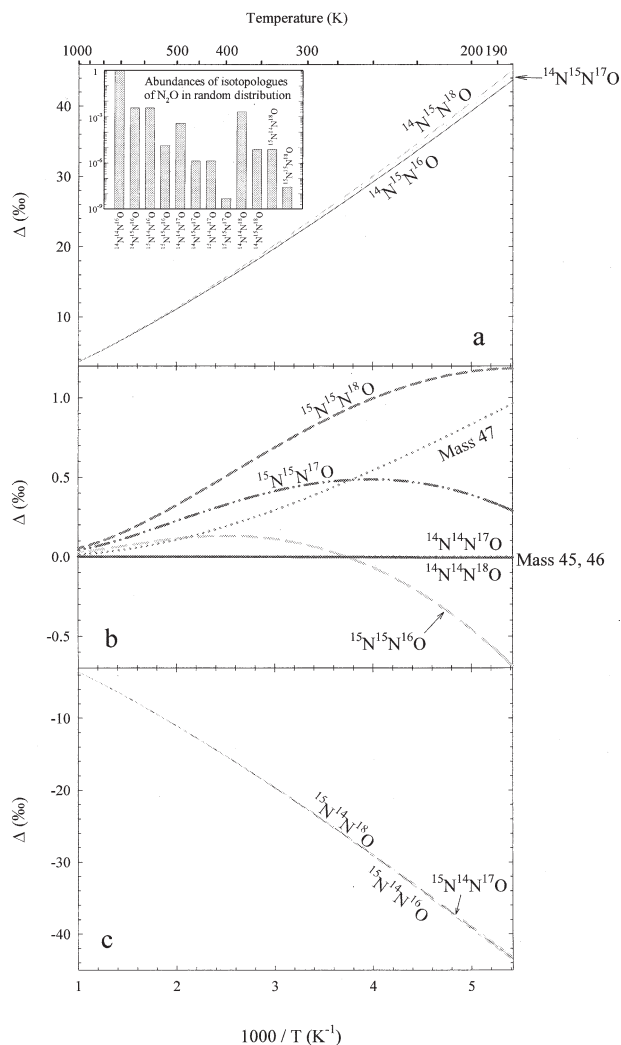
Fig. 7. (a) Variation of Δ values of isotopologues $^{14}N^{15}N^xO$, where x = 16,17, or 18, with 1/T; the inset shows the abundances of all isotopologues of N_2O for the stochastic distribution, a $^{15}N/^{14}N$ ratio equal to atmospheric N_2, and an oxygen isotope ratio equal to VS-MOW. (b) Variation of Δ values of isotopologues $^{14}N^{14}N^xO$, where x = 17 or 18, and $^{15}N^{15}N^xO$, where x= 16,17, or 18, with 1/T. C: Variation of Δ values of isotopologues, $^{15}N^{14}N^xO$, where x = 16,17, or 18, with 1/T.

Fig. 8. (a) Variation of $-1000 \cdot \ln(K_i/K_{i\text{-}random})$ (i = 8) with 1000/T for the isotope exchange reaction in Eqn. 35viii. (b) Variation of $-1000 \cdot \ln(K_i/K_{i\text{-}random})$ (i = 1 to 7) with 1000/T for the isotope exchange reactions in Eqn. 35i through 35vii.

tively (where x = 16, 17, 18). We speculate that similarly complex and large enrichments and depletions exist for other triatomic and higher-order asymmetric molecules (i.e., those with highest symmetry of $C_{\infty v}$ among their isotopologues).

These results provide a framework for interpretation of the natural abundances of multiply substituted isotopologues. For example, contributions of processes involving low temperature, thermodynamically controlled isotopic exchange (e.g., air-sea and air-leaf water exchange of CO_2) could be identified as contributors to budgets of atmospheric gases. Moreover, the size and temperature dependence of Δ values of most multiply substituted isotopologues suggest they can be used as geothermometers. Such thermometers differ from more familiar ones based on differences in bulk stable isotopic composition between coex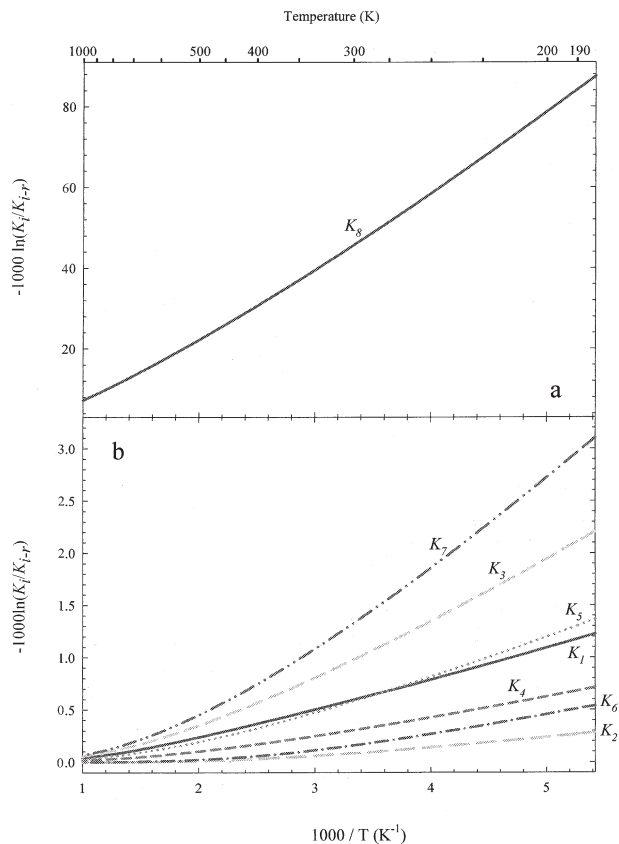isting phases; they instead involve homogeneous equilibria (e.g., isotopic distribution within a population of gaseous CO_2 molecules alone) and are effectively independent of bulk isotopic composition of that population. Furthermore, multiple independent thermometers exist for all molecules having more than one multiply substituted isotopologue (e.g., $^{18}O^{13}C^{16}O$ and $^{18}O^{12}C^{18}O$ for CO_2); thus, temperatures estimated by this method can be tested for internal consistency. Finally, the zero-point-energy differences between multiply substituted isotopologues and their isotopically "normal" and singly substituted relatives (Table 3) are also likely to manifest themselves in kinetic fractionations during nonequilibrium reactions (e.g., Yung and Miller, 1997). Our calculations provide guidance as to the sizes and directions of these effects.

It remains to be seen which of the isotope exchange reactions modeled here are manifested in natural atmospheric gases, other than initial evidence that $^{18}O^{13}C^{16}O$ in air is dominantly controlled by thermodynamic equilibrium (Eiler and Schauble, 2004). Furthermore, it must be determined which of these reactions resist continuous re-equilibration in the atmosphere and in the laboratory during sample preparation and analysis. Evidence to date suggests that such reequilibration does not occur for CO_2 over timescales of days to weeks at atmospheric pressures and temperatures and does not take place during most vacuum and gas-chromatography sample preparation techniques, nor during dual-inlet mass spectrometry (Eiler and

Schauble, 2004). Further work will be needed to establish whether this also holds true of other common molecular gases.

Measurements of multiply substituted isotopologues place special demands on techniques of sample preparation and mass spectrometry. These are detailed by Eiler and Schauble (2004). Briefly, they include (1) enough multiple static collectors to simultaneously measure isotopically "normal", singly substituted, and multiply substituted isotopologues (e.g., for CO_2, at least four collectors are needed and six are preferred); (2) high sensitivity (e.g., ability to stably register ion beams for species making up ca. 5–50 ppm of ca. μmolar samples) and high precision ($1\sigma < 0.1‰$). Fortunately, commonly available faraday cups and counting systems, when appropriately configured and read through 10^{12} Ohm resistors, appear to be sufficient for this task; (3) sample preparation procedures that remove potential interferences from other common molecular gases (e.g., $^{16}O_3$ on $^{18}O^{12}C^{18}O$) and, more problematically, halocarbons and hydrocarbons; and finally (4) as with more familiar measurements of singly substituted isotopologues, measurements of some multiply substituted isotopologues must be ion-corrected to account for "internal isobars" of one isotopologue of the analyte gas on another (e.g., $^{16}O^{13}C^{18}O$ and $^{17}O^{12}C^{18}O$ for CO_2). We are not aware of any instrument capable of resolving these isobars and also capable of high-precision measurements of isotope ratios. Therefore, at present, all such isobars are corrected for following procedures similar to the ^{17}O correction applied to conventional measurements of $\delta^{13}C$ of CO_2 (Santrock et al., 1985 and references therein). The related problem of resolving isotopomers (e.g., $^{14}N^{15}N^{18}O$ vs. $^{15}N^{14}N^{18}O$) should be addressable by either (1) spectroscopic methods (e.g., Yung and Miller, 1997), or (2) mass spectrometry of fragments (e.g., by monitoring $^{15}N^{18}O$ and $^{14}N^{18}O$ fragments during analysis of N_2O).

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APPENDIX

The calculations presented in section 3 of this study are based on several approximations made in the derivation of the Urey equation and its quantum-mechanical relatives. In this appendix, we present several calculations using higher-order theory made to test the accuracy of the harmonic oscillator and rigid rotor models. We make these tests for CO and CO_2 because their spectroscopic properties are relatively well known.

Alternate Models for CO

Table A1 shows the calculated Δ value for each isotopologue of CO at select temperatures based on three different methods: (1) the harmonic oscillator model (i.e., Eqn. 11 in this paper); (2) an anharmonic model using the Pitzer (1953) treatment (i.e., Eqn. 14 through 17); and (3) a model in which each vibrotational partition function was calculated by numerical summation over several vibrational and rotational quantum energy levels using the following equation:

$$Q_{v,J}(T) = \sum_{v=0}\sum_{J=0}(2J+1)\cdot e^{\frac{-hcE(v,J)}{kT}} \quad \text{(A-1)}$$

Input data for the first two methods are listed in Table 1 and are taken from Huber and Herzberg (1979). Three different sets of constraints were used for the third method: (1) a model using five Dunham parameter equations, in which data from Table 1 and Eqn. 13 were used to calculate energy at each quantum level, with vibrational and rotational quantum numbers up to 70 and 200, respectively; (2) a model using a larger number of Dunham parameters. In particular, forty-three mass-independent Dunham parameters from Authier et al., (1993) were used to evaluate the energy for every isotopologue at each quantum level, including the zero point energy, and vibrational and rotational quantum numbers were calculated up to 70 and 200, respectively; and (3) a model based on the HITRAN database (High Resolution Transmission), HITRAN2k (Rothman et al., 2003). This database compiles 4477 transmissions between low- and high-energy states of all six isotopologues of the CO molecule, and from which we can deduce the energy of each state involved. The line list for CO molecule in this database is mainly from Goorvitch (1994), modified to incorporate experimental data from Varberg and Evenson (1992). The zero point energy from Goorvitch (1994) was also adopted. After calculating the energy levels at each quantum number, Eqn. A-1 and Eqn. 18 were

used to calculate the full partition function. Results of these calculations summarized in Table A1 indicate that differences between these models are effectively irrelevant for our purposes.

We also explored the number of energy levels required to calculate $-1000\cdot\ln K_i$ ($i = 1,2$) in Eqn. 32i and 32ii at 1000 K. Forty-three Dunham parameters were used for this test. As shown in Figure A1-A and B, values of $-1000\cdot\ln K_i$ ($i = 1,2$) converge to within $0.05\permil$ when vibrational energy levels are larger than 2 and rotational energy levels are larger than 60. At lower temperatures, an even smaller number of energy levels is required for convergence.

Alternate Models for CO_2

The spectroscopic properties of CO_2 are relatively well studied, but remain incomplete. Rothman et al. (1992) present spectroscopic data for eight isotopologues: $^{16}O^{12}C^{16}O$ (155 vibrational energy levels); $^{16}O^{13}C^{16}O$ (78 vibrational energy levels); $^{16}O^{12}C^{18}O$ (59 vibrational energy levels); $^{16}O^{12}C^{17}O$ (26 vibrational energy levels); $^{16}O^{13}C^{18}O$ (16 vibrational energy levels); $^{16}O^{13}C^{17}O$ (10 vibrational energy levels); $^{18}O^{12}C^{18}O$ (12 vibrational energy levels); $^{17}O^{12}C^{18}O$ (3 vibrational energy levels). These data are insufficient for a full analysis of Δ values for most multiply substituted isotopologues. However, the 16 known energy levels for $^{16}O^{13}C^{18}O$ are better than other multiply substituted isotopologues and sufficient for a first-order analysis. We calculated the rotational energy for each vibration level using spectroscopic constants B_v, D_v, and H_v as follows:

$$E(v,J) = G_0 + G_v + B_vJ(J+1) - D_v[J(J+1)]^2 + H_v[J(J+1)]^3$$
$$\text{(A-2)}$$

Where G_0 is zero point energy listed in Table 3, G_v is the energy at each vibrational level with $J = 0$, and G_v, B_v, D_v, and H_v are listed in Rothman et al. (1992). Partition functions are directly summed over given vibrational quantum energy levels and calculated rotational quantum energy levels, with J up to 200 using an equation similar to Eqn. A-1, but including other factors:

$$Q_{v,J}(T) = \sum_{v_1,v_2,v_3=0}\sum_{l}^{v_2}g_{vl}g_{NS}\sum_{N}[2(N+l)+1]\cdot e^{\frac{-hcE(v,J)}{kT}} \quad \text{(A-3)}$$

where v_1, v_2, and v_3 are quantum numbers of three fundamental vibrational modes (please refer to Rothman and Young (1981) for notation details); l and N are angular momentum quantum numbers; l can take values of v_2, v_2-2, v_2-4, . . . , 1 or 0 and N can take any nonnegative integer; the sum of vector $\vec{l}$ and $\vec{N}$ is the total angular momentum vector $\vec{J}$, i.e., $\vec{J} = \vec{N} + \vec{l}$, therefore total angular momentum quantum number J can take possible values of $(N + l)$, $(N + l$-1), $\cdots$, $|N - l|$. Here the maximum of J (i.e., $J = N + l$) is chosen, which can take values of J, $(J$-1$)$, $(J$-2$)$,...,$-J$, contributing to $2J + 1$ degeneracy; g_{NS} is statistical weight caused by nuclear spin, and generally composed of two parts: (1) nuclear spin degeneracy factor for unpaired nuclei, this factor is $(2I_1+1)(2I_2+1)(2I_3+1)$ and same for all levels of a molecule (where I_i denotes the nuclear spin number of atom i), therefore will be cancelled out during the calculation of equilibrium constants; we ignored this part during our calculation of partition function; (2) nuclear spin degeneracy factor for coupling of equivalent nuclear pairs with rotational wavefunctions, this factor may differ between alternate rotational levels of one isotopologue, and therefore is included in our calculation of partition function (Herzberg, 1945; Gamache et al., 1990); since our consideration excludes $^{17}OC^{17}O$ isotopologues due to the lack of spectroscopic data of them, g_{NS} is 1 or 0 depending on the symmetric or antisymmetric rotational energy levels: i.e., when 2 oxygen atoms are the same isotopes (point group $D_{\infty h}$), $g_{NS} = 1$ for symmetric rotational states (N is even integer, e.g., 0,2,4, $\cdots$) and $g_{NS} = 0$ for antisymmetric rotational states (N is odd integer, e.g., 1,3,5, $\cdots$); otherwise, when 2 oxygen atoms are different isotopes (point group $C_{\infty v}$), $g_{NS} = 1$ for both symmetric and antisymmetric rotational states; g_{vl} is a statistical weight factor due to internal rotation, $g_{vl} = 1$ when $l = 0$ and $g_{vl} = 2$ when $l >0$.

Results of these calculations are shown in Figure A2-A for temperatures from 75 to 1000 K. Deviation in $-1000\cdot\ln K_3$ from that calculated using the "Urey" method (Eqn. 11 through 13) is small ($<0.1\permil$) below 260 K,

Table A1. Comparison of calculated Δ_i for CO molecule at select temperature using three methods (please refer to text for details).

Temperature (K)	Harmonic approximation					Anharmonic approximation				
	$^{13}C^{16}O$	$^{12}C^{17}O$	$^{12}C^{18}O$	$^{13}C^{17}O$	$^{13}C^{18}O$	$^{13}C^{16}O$	$^{12}C^{17}O$	$^{12}C^{18}O$	$^{13}C^{17}O$	$^{13}C^{18}O$
100	−0.0172	−0.0444	−0.0853	3.9421	7.5867	−0.0172	−0.0444	−0.0853	3.9392	7.5812
150	−0.0106	−0.0274	−0.0525	2.4292	4.6691	−0.0106	−0.0274	−0.0525	2.4268	4.6646
200	−0.0073	−0.0189	−0.0362	1.6735	3.2134	−0.0073	−0.0188	−0.0361	1.6714	3.2094
250	−0.0053	−0.0138	−0.0263	1.2206	2.3415	−0.0053	−0.0137	−0.0263	1.2187	2.3378
300	−0.0040	−0.0104	−0.0198	0.9197	1.7623	−0.0040	−0.0103	−0.0198	0.9179	1.7589
400	−0.0024	−0.0062	−0.0118	0.5503	1.0523	−0.0024	−0.0062	−0.0118	0.5487	1.0491
500	−0.0015	−0.0039	−0.0074	0.3429	0.6544	−0.0015	−0.0038	−0.0073	0.3415	0.6516
600	−0.0009	−0.0025	−0.0047	0.2202	0.4194	−0.0009	−0.0025	−0.0047	0.2190	0.4171
700	−0.0006	−0.0016	−0.0031	0.1453	0.2763	−0.0006	−0.0016	−0.0031	0.1444	0.2746
800	−0.0004	−0.0011	−0.0021	0.0985	0.1870	−0.0004	−0.0011	−0.0021	0.0978	0.1859
900	−0.0003	−0.0008	−0.0015	0.0684	0.1299	−0.0003	−0.0008	−0.0015	0.0681	0.1293
1000	−0.0002	−0.0005	−0.0010	0.0487	0.0924	−0.0002	−0.0005	−0.0010	0.0487	0.0924

| Temperature (K)	5 parameter Dunham equation					43 Dunham parameters					HITRAN data calculation				
	$^{13}C^{16}O$	$^{12}C^{17}O$	$^{12}C^{18}O$	$^{13}C^{17}O$	$^{13}C^{18}O$	$^{13}C^{16}O$	$^{12}C^{17}O$	$^{12}C^{18}O$	$^{13}C^{17}O$	$^{13}C^{18}O$	$^{13}C^{16}O$	$^{12}C^{17}O$	$^{12}C^{18}O$	$^{13}C^{17}O$	$^{13}C^{18}O$
100	−0.0172	−0.0444	−0.0853	3.9413	7.5852	−0.0172	−0.0444	−0.0853	3.9412	7.5849	−0.0172	−0.0444	−0.0853	3.9412	7.5823
150	−0.0106	−0.0274	−0.0525	2.4287	4.6682	−0.0106	−0.0274	−0.0525	2.4281	4.6670	−0.0106	−0.0274	−0.0525	2.4281	4.6654
200	−0.0073	−0.0189	−0.0361	1.6733	3.2131	−0.0073	−0.0189	−0.0361	1.6724	3.2113	−0.0073	−0.0189	−0.0361	1.6724	3.2100
250	−0.0053	−0.0138	−0.0263	1.2207	2.3417	−0.0053	−0.0137	−0.0263	1.2195	2.3393	−0.0053	−0.0137	−0.0263	1.2195	2.3383
300	−0.0040	−0.0104	−0.0198	0.9202	1.7633	−0.0040	−0.0104	−0.0198	0.9186	1.7603	−0.0040	−0.0104	−0.0198	0.9186	1.7595
400	−0.0024	−0.0062	−0.0119	0.5518	1.0552	−0.0024	−0.0062	−0.0118	0.5496	1.0510	−0.0024	−0.0062	−0.0118	0.5496	1.0504
500	−0.0015	−0.0039	−0.0074	0.3456	0.6596	−0.0015	−0.0039	−0.0074	0.3428	0.6542	−0.0015	−0.0039	−0.0074	0.3428	0.6537
600	−0.0010	−0.0025	−0.0048	0.2238	0.4266	−0.0010	−0.0025	−0.0047	0.2205	0.4201	−0.0010	−0.0025	−0.0047	0.2203	0.4196
700	−0.0006	−0.0017	−0.0032	0.1499	0.2853	−0.0006	−0.0016	−0.0031	0.1459	0.2776	−0.0006	−0.0016	−0.0031	0.1443	0.2763
800	−0.0004	−0.0012	−0.0022	0.1037	0.1974	−0.0004	−0.0011	−0.0021	0.0992	0.1886	−0.0004	−0.0010	−0.0021	0.0911	0.1834
900	−0.0003	−0.0008	−0.0016	0.0743	0.1414	−0.0003	−0.0008	−0.0015	0.0693	0.1315	−0.0003	−0.0005	−0.0013	0.0421	0.1142
1000	−0.0002	−0.0006	−0.0012	0.0552	0.1050	−0.0002	−0.0006	−0.0011	0.0495	0.0939	−0.0001	0.0002	−0.0005	−0.0208	0.0483
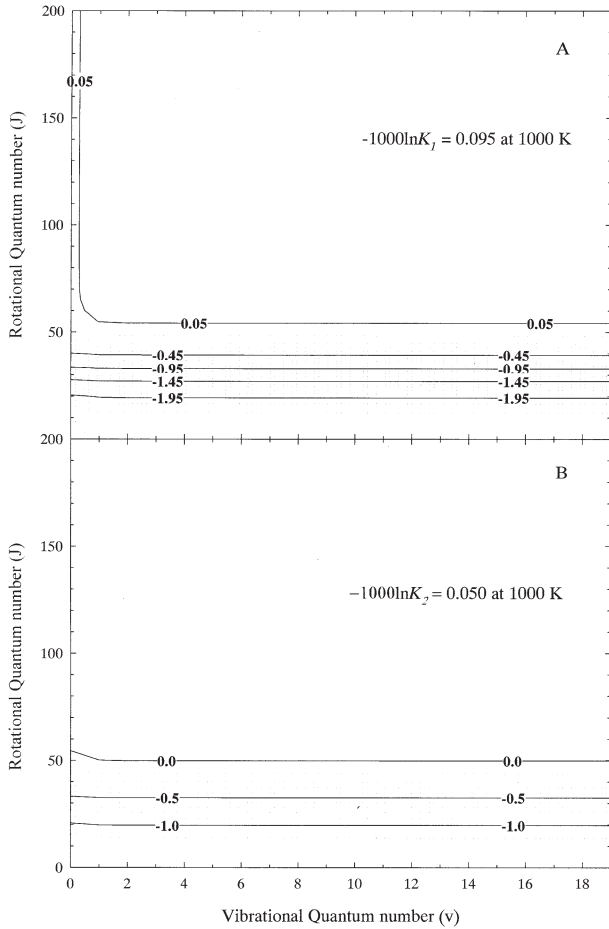
Fig. A1. Sensitivity test for the value of A: $-1000 \cdot \ln K_1$ and B: $-1000 \cdot \ln K_2$ in Eqn. 32i and 32ii as a function of maximum vibrational and rotational quanta calculated.
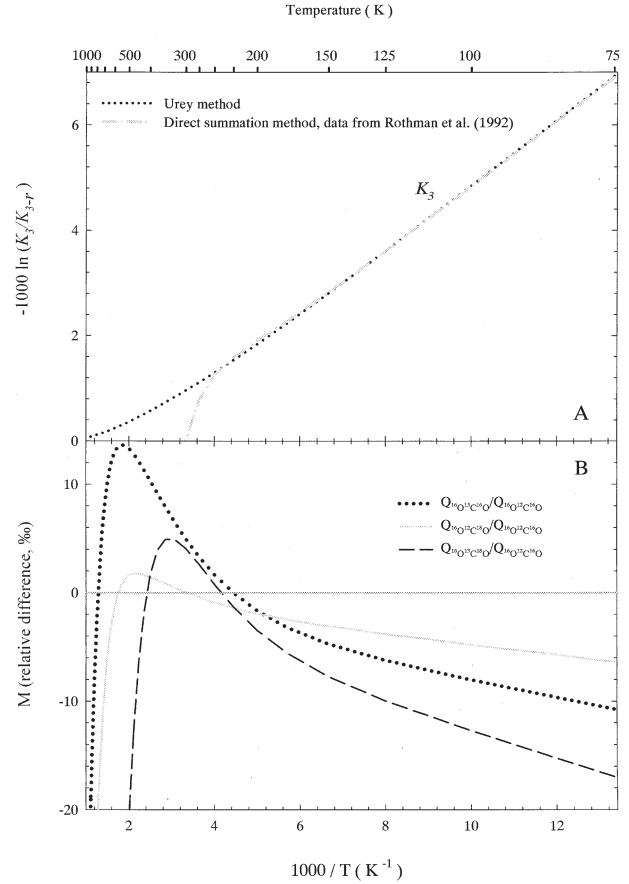

Fig. A2. A: Comparison of $-1000 \cdot \ln(K_3/K_{3-r})$ in Eqn. 8iii calculated using Urey method with using direct summation method as a function of 1000/T; B: Relative difference M_i (defined in equation A-5) between partition function ratios calculated using Urey method and direct summation method as a function of 1000/T.

but significant at higher temperatures. We suspect this reflects the absence of spectroscopic data for high-energy quantum states for $^{16}O^{13}C^{18}O$, and we conclude that the approximations associated with the Urey model are sufficiently accurate for our purposes.

Comparison also has been made for partition function ratios between calculations using these two methods. We use Eqn. 38 and 18 to calculate partition function of each isotopologue of $^{16}O^{12}C^{16}O$, $^{16}O^{13}C^{16}O$, $^{16}O^{12}C^{18}O$, and $^{16}O^{13}C^{18}O$. To calculate the right partition function ratio, we have to multiply Eqn. $\prod_i^n m_i^{\frac{3}{2}}$ according to the Teller-Redlich product rule (refer to Davidson, 1962), where m_i is the mass of atom i of n atoms that form the molecule, i.e.,

$$
\left(\frac{Q_{16_O13_C16_O}}{Q_{16_O12_C16_O}} \right)
$$

$$
= \left(\frac{m_{13_C}}{m_{12_C}} \right)^{\frac{3}{2}} \frac{\sigma_{16_O12_C16_O}}{\sigma_{16_O13_C16_O}} \prod_{i=1}^{3n-5} \frac{u_i^{16_O13_C16_O}}{u_i^{16_O12_C16_O}} \frac{e^{-\frac{u_i^{16_O13_C16_O}}{2}}}{1 - e^{-u_i^{16_O13_C16_O}}} \frac{1 - e^{-u_i^{16_O12_C16_O}}}{e^{-\frac{u_i^{16_O12_C16_O}}{2}}}
$$

$$(A-4)$$

We omit this factor in Eqn. 12 because this factor will be eventually cancelled out during the calculation of equilibrium constants. We define M as the relative difference in per mill between partition function ratios calculated using direct summation method and Urey's method as:

$$
M_i = \left(\frac{(Q_i/Q_{16_O12_C16_O})_{Numerical}}{(Q_i/Q_{16_O12_C16_O})_{Urey}} - 1 \right) \times 1000 \qquad (A-5)
$$

Where $i = {}^{16}O^{13}C^{16}O$, $^{16}O^{12}C^{18}O$, and $^{16}O^{13}C^{18}O$. Figure A2-B shows the difference between these two model changes with temperature. To the first order, there is a difference of up to 20‰ between these two methods at temperatures lower than 500 K, and the deviation in $-1000 \cdot \ln K_3$ between two models can be approximated into $M_{16_O13_C18_O} - M_{16_O13_C16_O} - M_{16_O12_C18_O}$ within 0.1‰. As we can see in Figure A2-B, even though individual M_i is up to $-19‰$ at temperatures lower than 250 K, the deviation in $-1000 \cdot \ln K_3$ is smaller than 0.1‰. This difference seems to be qualitatively correlative to the number of vibrational levels used in the direct summation calculation. With increasing temperatures higher than 300 K, $Q_{16_O13_C18_O}$ began to show progressively higher deviation from the Urey method. This is caused by a greater contribution from the higher vibrational energy levels of $^{16}O^{13}C^{18}O$, for which information is not yet available. Especially, the lack of several vibrational energy levels from 2000 cm^{-1} to 3000 cm^{-1} (e.g., 11102 e,f and 03301 e,f; notations follow Rothman and Young (1981) and Rothman et al. (1992)) during the calculation will reduce the value of $\frac{Q_{16_O13_C18_O}}{Q_{16_O12_C16_O}}$, even at low temperatures (<300 K), and therefore, reduce the value of $-1000 \cdot \ln K_3$. Hence, we believe that the deviation of $-1000 \cdot \ln K_3/K_{3-r}$ calculated using the direct summation method from the calculation result of the Urey method shown in Figure A2-A is due to the insufficiency of vibrational energy levels known for isotopologue $^{16}O^{13}C^{18}O$, rather than due to the calculation method, and we conclude that the approximations associated with the Urey model are sufficiently accurate for our purposes.