



## RESEARCH LETTER

10.1002/2015GL066438

## Key Points:

- Nitrogen isotope exchange fractionation between NO and NO<sub>2</sub> was measured
- Experimental measurements agree with theoretical calculated values
- Implications for δ<sup>15</sup>N variations in atmospheric NO<sub>x</sub> and nitrate

## Supporting Information:

- Supporting Information S1

## Correspondence to:

W. W. Walters  
waltersw@purdue.edu

## Citation:

Walters, W. W., D. S. Simonini, and G. Michalski (2016), Nitrogen isotope exchange between NO and NO<sub>2</sub> and its implications for δ<sup>15</sup>N variations in tropospheric NO<sub>x</sub> and atmospheric nitrate, *Geophys. Res. Lett.*, *43*, 440–448, doi:10.1002/2015GL066438.

Received 2 OCT 2015

Accepted 9 DEC 2015

Accepted article online 12 DEC 2015

Published online 6 JAN 2016

## Nitrogen isotope exchange between NO and NO<sub>2</sub> and its implications for δ<sup>15</sup>N variations in tropospheric NO<sub>x</sub> and atmospheric nitrate

Wendell W. Walters<sup>1</sup>, Damian S. Simonini<sup>2</sup>, and Greg Michalski<sup>1,2</sup>

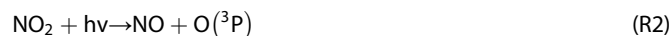
<sup>1</sup>Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, West Lafayette, Indiana, United States,

<sup>2</sup>Department of Chemistry, Purdue University, West Lafayette, Indiana, United States

**Abstract** The nitrogen (N) isotope exchange between nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) has been previously suggested to influence N stable isotope compositions (δ<sup>15</sup>N) of these molecules. However, there is disagreement in the magnitude of the N isotopic fractionation (α<sub>NO<sub>2</sub>/NO</sub>) resulting from this exchange process between previous experimental and theoretical studies. To this end, we measured α<sub>NO<sub>2</sub>/NO</sub> associated with this exchange reaction at various temperatures. Our results indicate α<sub>NO<sub>2</sub>/NO</sub> to be 1.0403 ± 0.0015, 1.0356 ± 0.0015, and 1.0336 ± 0.0014 at 278 K, 297 K, and 310 K, respectively. These measured values are within experimental error of the values we calculated using a modified version of the Bigeleisen-Mayer equation corrected for accurate zero-point energies, indicating an agreement between experiment and theory. Modeling of this exchange reaction demonstrates that δ<sup>15</sup>N-NO<sub>2</sub> may exhibit a diurnal and seasonal profile if N isotopic equilibrium is achieved.

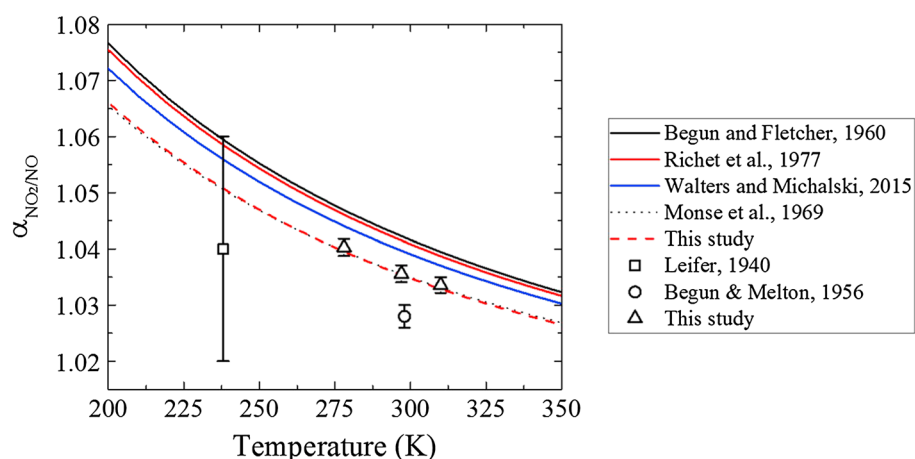
### 1. Introduction

Nitrogen oxides [NO<sub>x</sub> = nitric oxide (NO) + nitrogen dioxide (NO<sub>2</sub>)] are important trace gases that influence the concentrations of the major tropospheric oxidants including ozone (O<sub>3</sub>) and hydroxyl radical (OH) that drive tropospheric chemistry [Leighton, 1961; Crutzen, 1973, 1979; Logan, 1983]. During the daytime, NO and NO<sub>2</sub> exist in a photochemical steady state in which NO is oxidized by O<sub>3</sub> forming NO<sub>2</sub>, which then may photolyze back to NO leading to the production of O<sub>3</sub> [Leighton, 1961]. This cycling of NO and NO<sub>2</sub> is known as the Leighton cycle and is described by the following reaction sequence [Leighton, 1961]:



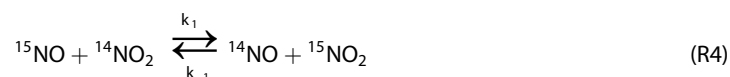
The cycling between NO and NO<sub>2</sub> is relatively rapid with photochemical equilibrium being achieved within a few minutes [Freyer *et al.*, 1993; Seinfeld and Pandis, 2006]. Thus, during the daytime, the Leighton cycle controls the relative concentrations of NO and NO<sub>2</sub> depending on O<sub>3</sub> concentrations and NO<sub>2</sub> photolysis rate.

The nitrogen (N) isotope exchange equilibrium between NO and NO<sub>2</sub> has been suggested to play an important role in the <sup>15</sup>N/<sup>14</sup>N ratios of NO and NO<sub>2</sub> [Freyer *et al.*, 1993] and atmospherically derived nitrate: nitric acid (HNO<sub>3</sub>), nitrate (NO<sub>3</sub><sup>-</sup>), and particulate nitrate (p-NO<sub>3</sub><sup>-</sup>) [Riha, 2013; Savarino *et al.*, 2013]. The partitioning of <sup>15</sup>N between NO and NO<sub>2</sub> depends on their relative concentration (NO/NO<sub>x</sub> and NO<sub>2</sub>/NO<sub>x</sub>) and the temperature-dependent isotope equilibrium fractionation factor [Freyer *et al.*, 1993]. During the daytime, when near equal concentrations of NO and NO<sub>2</sub> coexist due to the Leighton cycle, the N isotope exchange between NO and NO<sub>2</sub> has been suggested to influence their individual <sup>15</sup>N/<sup>14</sup>N ratios via the equilibrium isotope effect [Freyer *et al.*, 1993]. During the nighttime, however, NO concentrations may approach zero if O<sub>3</sub> concentrations are high, as NO is oxidized into NO<sub>2</sub> ((R1)) without photolyzing back to NO ((R2)) [Rinsland *et al.*, 1984; Freyer *et al.*, 1993]. Under these conditions, the NO<sub>2</sub> in the atmosphere likely reflects <sup>15</sup>N/<sup>14</sup>N ratios of local NO<sub>x</sub> sources [Freyer *et al.*, 1993]. Therefore, this isotope exchange reaction has important implications for using the N stable isotope composition of atmospheric nitrate to partition NO<sub>x</sub> sources [Heaton, 1987; Freyer, 1991; Elliott *et al.*, 2007, 2009] or as a chemical tracer of atmospheric processes [Freyer, 1978, 1991; Heaton, 1987; Freyer *et al.*, 1993; Savarino *et al.*, 2013; Walters and Michalski, 2015].



**Figure 1.** Comparison between previous theoretical calculations of  $\alpha_{\text{NO}_2/\text{NO}}$  using harmonic frequencies (solid lines), observable vibrational frequencies (dotted line), harmonic frequencies corrected for anharmonic zero-point energies (dashed line), and experimental measurements (square, circle, and triangle points).

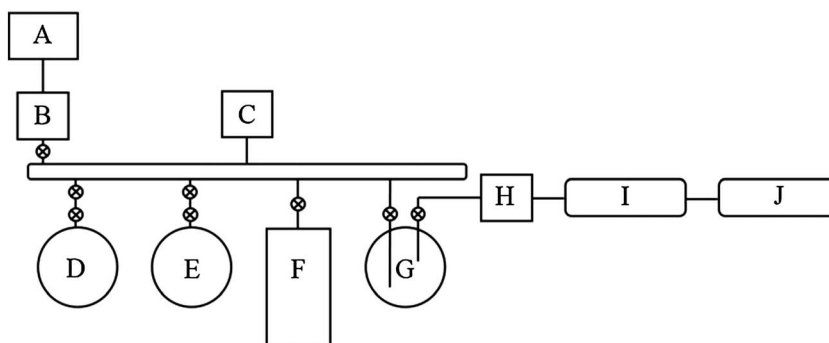
N isotope exchange between NO and  $\text{NO}_2$  (R4) has equilibrium constant ( $K = k_1/k_{-1}$ )



that depends on the thermodynamic differences between the N isotopologues of NO and  $\text{NO}_2$  [Urey, 1947]. In the Born-Oppenheimer approximation, differences in the thermodynamics of an isotopologue pair depend on the isotopologue-dependent vibrational frequencies [Urey, 1947]. Substitution of a heavier isotope will lower the vibrational frequency and the vibrational zero-point energy (ZPE) of a molecule. Based on N isotopologue ZPEs, R4 is favored to the right as the ZPE is lower on the right side (ZPE = 32.39 kJ/mol) than for the left (ZPE = 33.56 kJ/mol) [Begun and Fletcher, 1960], indicating that  $^{15}\text{N}$  will preferentially form in  $\text{NO}_2$  over NO.

While the NO and  $\text{NO}_2$  exchange favoring the formation of  $^{15}\text{NO}_2$  has been observed in experimental measurements [Leifer, 1940; Begun and Melton, 1956] and predicted by theoretical calculations [Begun and Fletcher, 1960; Monse et al., 1969; Richet et al., 1977; Walters and Michalski, 2015], there is disagreement between theoretical and experimental studies on the value of the equilibrium constant, also called the fractionation factor ( $\alpha$ ) (Figure 1). Using the Bigeleisen-Mayer equation in the harmonic oscillator approximation [Bigeleisen and Mayer, 1947; Urey, 1947], theoretical studies have predicted fractionation factors for  $^{15}\text{N}$  substitution between  $\text{NO}_2$  and NO ( $\alpha_{\text{NO}_2/\text{NO}}$ ) to range from 1.0354 to 1.042 at 298 K [Begun and Fletcher, 1960; Monse et al., 1969; Richet et al., 1977; Walters and Michalski, 2015]. However, these predicted values are substantially different than the experimental  $\alpha_{\text{NO}_2/\text{NO}}$  of  $1.028 \pm 0.002$  at 298 K [Begun and Melton, 1956]. At 238 K, theory predicts  $\alpha_{\text{NO}_2/\text{NO}}$  to range from 1.0552 to 1.0596 [Begun and Fletcher, 1960; Richet et al., 1977; Walters and Michalski, 2015]. Experimental  $\alpha_{\text{NO}_2/\text{NO}}$  at 238 K has been measured to be  $1.040 \pm 0.02$  [Leifer, 1940], technically within experimental error of the theoretical value, but with a relative large uncertainty.

The disagreement between experiment and theory might be due to the analytical method used to measure the abundances of the N isotopologues of NO and  $\text{NO}_2$ . The mass spectrometer technique used to measure  $\text{NO}_2$  is subject to mass interference via the formation of  $\text{NO}^+$  and  $\text{NO}_2^+$  ions that originate from  $\text{NO}_2$  [Leifer, 1940; Begun and Melton, 1956]. Disagreements could also be related to the harmonic approximation used to calculate the theoretical  $\alpha_{\text{NO}_2/\text{NO}}$  values as inclusion of anharmonicity will tend to lower  $\alpha_{\text{NO}_2/\text{NO}}$  values [Liu et al., 2010]. In this study, we will revisit the N isotope exchange between NO and  $\text{NO}_2$  using measurement techniques that will overcome previous experimental measurement limitations in an effort to reconcile previous experimental and theoretical differences for this isotope exchange reaction.



**Figure 2.** Experimental setup for the N isotopic exchange between NO and NO<sub>2</sub>. The symbols are A = rotary pump, B = diffusion pump, C = vacuum gage, D = NO bulb ( $\delta^{15}\text{N} = -42.5\%$ ), E = NO<sub>2</sub> bulb ( $\delta^{15}\text{N} = -32.0\%$ ), F = Argon tank (>99.5%), G = 1 L reaction vessel, H = flow meter, I = NO<sub>2</sub> binding denuder tube, and J = NO<sub>2</sub> breakthrough denuder tube.

## 2. Methods

### 2.1. Experiment Design

The experiment utilized a reaction vessel, vacuum line, and a series of denuder tubes (Figure 2). A 1 L two-necked reaction vessel was attached to one end of the vacuum line and a series of denuder tubes were connected to the other end. A NO bulb ( $\delta^{15}\text{N} = (-42.5 \pm 0.9)\%$ ), NO<sub>2</sub> bulb ( $\delta^{15}\text{N} = (-32.0 \pm 0.9)\%$ ), and a high-purity argon (Ar) tank (>99.5%) were connected to the vacuum line inlet ports using ultratorr fittings. Here  $\delta^{15}\text{N}(\%) = [(^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{air}} - 1] \times 1000$ . The reaction vessel and vacuum line was evacuated to  $10^{-4}$  Pa and then a mixture of roughly 6.70 Pa of NO and 27.0 Pa of NO<sub>2</sub> was introduced into the system. The reaction vessel was sealed off from the vacuum line, and the vacuum line was then evacuated back down to  $10^{-4}$  Pa. The vacuum line was isolated and high-purity Ar was introduced into the vacuum line and bled into the reaction vessel until a pressure of 101.3 kPa was achieved. The NO and NO<sub>2</sub> pressures were kept low in order to prevent appreciable formation of N<sub>2</sub>O<sub>3</sub> or N<sub>2</sub>O<sub>4</sub> molecules. With the pressures of NO and NO<sub>2</sub> used in this experiment, we calculated N<sub>2</sub>O<sub>3</sub> pressures to be less than 2.05 mPa using the NO + NO<sub>2</sub> ↔ N<sub>2</sub>O<sub>3</sub> equilibrium constant [Verhoek and Daniels, 1931] and less than 16.6 mPa for N<sub>2</sub>O<sub>4</sub> using 2NO<sub>2</sub> ↔ N<sub>2</sub>O<sub>4</sub> equilibrium constant [Hurtmans *et al.*, 1993] (calculations in supporting information). Therefore, N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>4</sub> formation should be negligible in our experimental setup.

The NO/NO<sub>2</sub> mixture was allowed to equilibrate for 5 min, and then NO<sub>2</sub> was collected using the denuder tubes. The N isotope exchange rate between NO and NO<sub>2</sub> has been previously measured to be  $8.14 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  [Sharma *et al.*, 1970]. Kinetic modeling of this reaction indicates that N isotopic equilibrium should be reached in less than 1 s at the NO and NO<sub>2</sub> pressures used in this experiment; therefore, N isotopic equilibrium between NO and NO<sub>2</sub> will easily be achieved in the experimental setup. The NO and NO<sub>2</sub> were purged from the bulb by flowing Ar at a rate of 2 L/min for 10 min. The gases passed through a denuder tube (inner diameter = 3 mm and length = 1 m) coated with a 0.5 mL dried solution of 2.5 M potassium hydroxide and 25% by weight of guaiacol (C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>) using methanol as a solvent. This coated mixture selectively binds NO<sub>2</sub> as nitrite (NO<sub>2</sub><sup>-</sup>) [Williams and Grosjean, 1990; Ammann *et al.*, 1999; Li and Wang, 2008]. The denuder tube binding efficiency is based on the time for NO<sub>2</sub> to diffuse to the surface of the coated denuder tube, which depends on the flow rate, time to achieve laminar flow, and time for NO<sub>2</sub> to diffuse to the surface of the coated denuder tube [Ali *et al.*, 1989]. Mathematical modeling of these processes indicates that a tube length of 1 m will allow more than 99.9% of all NO<sub>2</sub> to be absorbed by the employed denuder tube and experimental conditions (i.e., flow rate and denuder diameter) [Ali *et al.*, 1989]. A second denuder tube was connected in series with the first tube to check for NO<sub>2</sub> breakthrough.

After sampling, the denuder tubes are separately rinsed with 3 mL of 18.2 MΩ Millipore water. Control tests using NO<sub>2</sub> pressures of 13.3 Pa (upper limit of actual NO<sub>2</sub> pressures used in exchange experiments) indicate that NO<sub>2</sub><sup>-</sup> in the second denuder tube was below the detection limit (100 ppb) of an Ion Chromatography (Dionex IonPac AS19). Additionally, the outflow from the second denuder tube was analyzed using a NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer (Thermo Scientific) and NO<sub>x</sub> was never detected above the background level. These control tests suggest that NO<sub>2</sub> breakthrough did not occur, and there is a negligible NO<sub>2</sub><sup>-</sup> blank in the

guaiacol/KOH binding salt. Nitrate ( $\text{NO}_3^-$ )/ $\text{NO}_2^-$  test strips (Aquacheck) indicated that  $\text{NO}_2^-$  in the second denuder tube was below the detection limit of 500 ppb in each of our exchange trials. Control tests using only the  $\text{NO}_2$  bulb that went through the entire  $\text{NO}_2$  binding procedure indicate that the reproducibility in our measured  $\delta^{15}\text{N}$ - $\text{NO}_2$  values to be  $-32.5 \pm 0.7\text{‰}$  ( $n = 5$ ), in excellent agreement with the N isotope composition of the  $\text{NO}_2$  bulb ( $-32.0\text{‰}$ ). Additionally, control tests using only the NO bulb indicate that NO does not bind onto the denuder tubes that are designed to specifically bind  $\text{NO}_2$ .

Five trials at three different temperatures (278 K, 297 K, and 310 K) were performed. Since the exchange rate between NO and  $\text{NO}_2$  is extremely fast ( $< 1$  s under experimental conditions), it was necessary to temperature control both the reaction vessel and the denuder tubes. For the trials at 278 K and 310 K, temperatures were controlled by submerging the reaction vessel and denuder tubes into an ice water (278 K) or hot water (310 K) bath. The reaction vessel and denuder tubes were allowed 10 min to equilibrate with the temperature of the water bath before each trial was performed. Temperatures were monitored throughout the experiment for each trial and indicate that the cold and hot water bath did not vary by more than 0.5 K for each individual trial and by no more than 1 K for the five trials at the same temperature. For the room temperature exchange (297 K), a water bath was not used, but the laboratory room temperature was monitored and did not vary by more than 0.5 K for each individual exchange and by no more than 1 K between the different trials.

## 2.2. N Isotopic Analysis

N isotopic analysis was performed on the product  $\text{NO}_2^-$  in the elutant from the first denuder tube for each exchange trial. Approximately 250 nmol of  $\text{NO}_2^-$  was converted into nitrous oxide ( $\text{N}_2\text{O}$ ) using sodium azide in an acetic acid buffer [McIlvin and Altabet, 2005]. The  $\text{N}_2\text{O}$  was extracted and purified using an automated headspace gas chromatography system and analyzed by a Thermo Delta V Continuous Flow Isotope Ratio Mass Spectrometer (GC-CF-IRMS) for  $m/z$  44, 45, and 46 at the Purdue Stable Isotopes Lab. Five working lab  $\text{NO}_3^-$  standards, calibrated to NIST isotope reference USGS34 and USGS35 were used to correct for isotopic fractionation associated with the  $\text{N}_2\text{O}$  purification process. Our working lab standards have the following  $\delta^{15}\text{N}$ (‰) relative to air:  $-20.0$ ,  $-7.6$ ,  $0.5$ ,  $10.6$ , and  $15.3$ . Before the working lab  $\text{NO}_3^-$  standards were converted to  $\text{N}_2\text{O}$  using the sodium azide and acetic acid buffer, they were first reduced to  $\text{NO}_2^-$  using an activated cadmium metal in a 5 M NaCl solution [Ryabenko et al., 2009]. Working lab standards had an average standard deviation of 0.5‰ for  $\delta^{15}\text{N}$ .

## 2.3. Experimental Determination of $\alpha_{\text{NO}_2/\text{NO}}$

The  $\alpha_{\text{NO}_2/\text{NO}}$  associated with N isotope exchange between NO and  $\text{NO}_2$  (R4) can be related by the abundances of  $^{14}\text{NO}$ ,  $^{15}\text{NO}$ ,  $^{14}\text{NO}_2$ , and  $^{15}\text{NO}_2$  at equilibrium:

$$K_{\text{NO}_2/\text{NO}} = \alpha_{\text{NO}_2/\text{NO}} = \frac{(^{15}\text{NO}_2)(^{14}\text{NO})}{(^{14}\text{NO}_2)(^{15}\text{NO})} = \left( \frac{^{15}\text{R}_{\text{NO}_2}}{^{15}\text{R}_{\text{NO}}} \right), \quad (1)$$

where  $^{15}\text{R} = ^{15}\text{N}/^{14}\text{N}$  ratios. Since initial  $^{15}\text{R}$  and pressures are known for NO and  $\text{NO}_2$ , mass-balance will enable us to calculate the total  $^{15}\text{R}$  in our equilibrium system:

$$^{15}\text{R}_{\text{Total}} = ^{15}\text{R}_{\text{NO}(i)} \cdot p_{\text{NO}} + ^{15}\text{R}_{\text{NO}_2(i)} \cdot p_{\text{NO}_2}, \quad (2)$$

where  $p$  is the partial pressure fraction (e.g.,  $p_{\text{NO}}/p_{\text{NO}_x}$ ) of either NO or  $\text{NO}_2$  and  $(i)$  denotes the initial  $^{15}\text{R}$  of either NO or  $\text{NO}_2$ . At equilibrium, we only measured  $^{15}\text{R}$  for  $\text{NO}_2$ ; however,  $^{15}\text{R}$  of NO at equilibrium can be calculated using our mass-balance relationship in equation (2):

$$^{15}\text{R}_{\text{NO}(e)} \cdot p_{\text{NO}} = ^{15}\text{R}_{\text{Total}} - ^{15}\text{R}_{\text{NO}_2(e)} \cdot p_{\text{NO}_2}, \quad (3)$$

where  $(e)$  denotes the equilibrium  $^{15}\text{R}$  of either NO or  $\text{NO}_2$ . Using the equilibrium  $^{15}\text{R}_{\text{NO}}$  and  $^{15}\text{R}_{\text{NO}_2}$ ,  $\alpha_{\text{NO}_2/\text{NO}}$  can be calculated from equation (1).

## 3. Results and Discussion

### 3.1. $\alpha_{\text{NO}_2/\text{NO}}$

The NO and  $\text{NO}_2$  pressures, measured  $\delta^{15}\text{N}$  of  $\text{NO}_2$  at equilibrium, and experimental determined  $\alpha_{\text{NO}_2/\text{NO}}$  values for each trial is reported in the supporting information. The experimental  $\alpha_{\text{NO}_2/\text{NO}}$  values were determined to be  $1.0403 \pm 0.0015$ ,  $1.0356 \pm 0.0015$ , and  $1.0336 \pm 0.0014$  at 278 K, 297 K, and 310 K, respectively.

These values are within experimental error of  $\alpha_{\text{NO}_2/\text{NO}}$  values calculated using GF matrix derived vibrational frequencies, where G is the a symmetric matrix set-up using the Wilson vector method and F is the force derivative matrix. [Monse *et al.*, 1969] in the Bigeleisen-Mayer equation (1.0396, 1.0355, and 1.0331 at 278 K, 297 K, and 310 K, respectively). In contrast, the experimental  $\alpha_{\text{NO}_2/\text{NO}}$  values tend to be slightly lower than the  $\alpha_{\text{NO}_2/\text{NO}}$  values theoretically calculated at these temperatures using experimental harmonic frequencies in the Bigeleisen-Mayer equation (1.0461, 1.0415, and 1.0387, respectively) [Richet *et al.*, 1977] and slightly lower than the values predicted using harmonic frequencies calculated using quantum mechanical methods (1.0441, 1.0397, and 1.03704, respectively) [Walters and Michalski, 2015] (Figure 1).

While our experimental  $\alpha_{\text{NO}_2/\text{NO}}$  agree well with the values calculated by Monse *et al.* [1969], there are some concerns in the way those values were calculated. In Monse *et al.* [1969], frequencies for the N isotopologues of NO and NO<sub>2</sub> were calculated using force fields observed from fundamental vibrational frequencies, and these computed frequencies were used to calculate  $\alpha_{\text{NO}_2/\text{NO}}$  using the Bigeleisen-Mayer equation. However, constructing the force fields of polyatomic molecules is complex and often requires several simplifications and approximations [Wilson *et al.*, 1955; Liu *et al.*, 2010]. Therefore, this method is not recommended to calculate isotope exchange  $\alpha$  values as it tends to result in larger errors relative to  $\alpha$  values calculated using harmonic frequencies [Liu *et al.*, 2010]. Thus, the agreement between our calculated  $\alpha_{\text{NO}_2/\text{NO}}$  values and the values calculated by Monse *et al.* [1969] might be fortuitous.

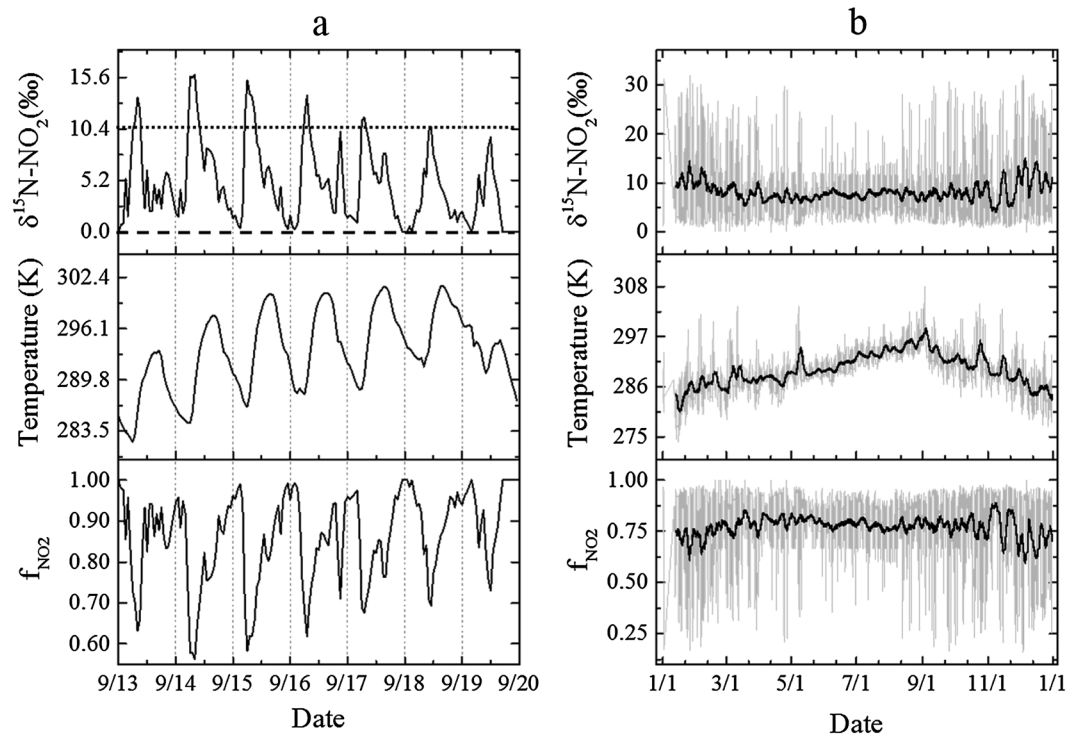
Theoretical predictions of isotope exchange processes using the Bigeleisen-Mayer equation can be improved by accounting for corrections for anharmonicity on the ZPE which can have a significant impact on  $\alpha$  values [Liu *et al.*, 2010]. To this end, we have calculated theoretical  $\alpha_{\text{NO}_2/\text{NO}}$  values using a modified version of the Bigeleisen-Mayer equation with anharmonic corrections for accurate zero-point energies [Liu *et al.*, 2010], using experimental harmonic frequencies for the N isotopologues of NO and NO<sub>2</sub> [Olman *et al.*, 1964; Blank and Hause, 1970] and experimental zero-point energies [Henry *et al.*, 1978; Teffo *et al.*, 1980; Michalski *et al.*, 2004] (Figure 1). Details on this calculation and our calculated  $\alpha_{\text{NO}_2/\text{NO}}$  regression parameters as a function of temperature for this exchange can be found in the supporting information. Using this approach, we calculated  $\alpha_{\text{NO}_2/\text{NO}}$  values of 1.0395, 1.0352, and 1.0329 at 278 K, 297 K, and 310 K, respectively, which is within the experimental uncertainty of our measurements (Figure 1).

Overall, there is excellent agreement between our theoretical calculated  $\alpha_{\text{NO}_2/\text{NO}}$  and our experimental measured values. Liefer's [1940] measured  $\alpha_{\text{NO}_2/\text{NO}}$  of  $1.040 \pm 0.020$  at 238 K is also in agreement with our theoretical calculated value of 1.0508 at 238 K, though the experimental uncertainty is relatively high. However, both our experimental and theoretical  $\alpha_{\text{NO}_2/\text{NO}}$  values disagree with the value reported by Begun and Melton [1956]. Begun and Melton determined  $\alpha_{\text{NO}_2/\text{NO}}$  to be  $1.028 \pm 0.002$  at 298 K [Begun and Melton, 1956], which is slightly lower than our experimental value of  $1.0356 \pm 0.0015$  at 297 K or our theoretical calculated value of 1.0352 at 298 K. The disagreement or relatively high uncertainty in these previous  $\alpha_{\text{NO}_2/\text{NO}}$  measurements may be explained due to the experimental measurement techniques. In both of these previous studies, the abundances of the N isotopologues of NO and NO<sub>2</sub> were measured by flowing gaseous NO and NO<sub>2</sub> into a mass spectrometer, but the separate mass analysis for the NO<sub>2</sub> and NO peaks is complicated due to the formation of NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup> ions that originate from NO<sub>2</sub> [Liefer, 1940; Begun and Melton, 1956]. This may have artificially lowered the abundance of <sup>15</sup>NO<sub>2</sub> and increased the abundance of <sup>15</sup>NO. In our experimental measurement technique, our samples were converted into a relatively inert gas (N<sub>2</sub>O) and <sup>15</sup>N/<sup>14</sup>N ratios were directly compared to N isotopic references, which should eliminate previous experimental measurement limitations. Therefore, we believe our data reconcile previous disagreements between experimental measurements and theoretical calculations for this N isotope exchange process and will be useful in interpreting <sup>15</sup>N/<sup>14</sup>N ratios of atmospheric NO and NO<sub>2</sub>.

### 3.2. Implications for $\delta^{15}\text{N}$ of Atmospheric NO<sub>2</sub>

In order to understand the impact the N isotope exchange between NO and NO<sub>2</sub> has on  $\delta^{15}\text{N}$ -NO<sub>2</sub>, we modeled the diurnal cycle and seasonal changes in  $\delta^{15}\text{N}$ -NO<sub>2</sub> (Figure 3), using a NO<sub>x</sub> mass-balance model assuming that NO and NO<sub>2</sub> achieve N isotopic equilibrium. The exchange  $\alpha_{\text{NO}_2/\text{NO}}$  can be related to  $\delta$  notation by the following:

$$\alpha_{\text{NO}_2/\text{NO}} = \left[ \frac{\delta^{15}\text{N-NO}_2 + 1000}{\delta^{15}\text{N-NO} + 1000} - 1 \right] \cdot 1000. \quad (4)$$



**Figure 3.** Hourly changes in  $\delta^{15}\text{N-NO}_2$ (‰) (assuming equilibrium between NO and  $\text{NO}_2$  is achieved), temperature (K), and  $f_{\text{NO}_2}$  (a) over a week at Indianapolis, IN, USA (13 September–20 September 2015) and (b) over a year (2007) at Chula Vista, CA, USA. “a” highlights the conditions that N isotope exchange has a strong influence on  $\delta^{15}\text{N-NO}_2$  relative to  $\delta^{15}\text{N-NO}_x$  (dotted line) and conditions that have little influence on  $\delta^{15}\text{N-NO}_2$  relative to  $\delta^{15}\text{N-NO}_x$  (dashed line). Heavy curves in “b” are 100 point (100 h) moving averages.

Here we define  $\delta^{15}\text{N}$  to be relative to the total  $\text{NO}_x$ , for example  $\delta^{15}\text{N-NO}_2$  is expressed as

$$\delta^{15}\text{N-NO}_2(\text{‰}) = \left[ \frac{^{15}\text{R}_{\text{NO}_2}}{^{15}\text{R}_{\text{NO}_x}} - 1 \right] \cdot 1000 \quad (5)$$

with  $\delta^{15}\text{N-NO}_x$  set to 0‰ relative to atmospheric air. Mass and isotopic balance for NO and  $\text{NO}_2$  results in the following relationship:

$$f_{\text{NO}_2} \cdot \delta^{15}\text{N-NO}_2 + f_{\text{NO}} \cdot \delta\text{N-NO} = 1 \cdot \delta^{15}\text{N-NO}_x = 0\text{‰}, \quad (6)$$

where  $f$  is mole fraction of NO or  $\text{NO}_2$  to the total  $\text{NO}_x$ . Combining equations (4)–(6) results in the following relationship between  $\delta^{15}\text{N-NO}_2$ ,  $\alpha_{\text{NO}_2/\text{NO}}$ , and  $f_{\text{NO}_2}$ :

$$\delta^{15}\text{N-NO}_2(0\text{‰}) = \left[ \frac{(\alpha_{\text{NO}_2/\text{NO}} - 1)(1 - f_{\text{NO}_2})}{(1 - f_{\text{NO}_2}) + (\alpha_{\text{NO}_2/\text{NO}} \cdot f_{\text{NO}_2})} \right]. \quad (7)$$

The mass-balance model highlights that the  $\delta^{15}\text{N-NO}_2$  value will change depending on  $f_{\text{NO}_2}$  and temperature-dependent  $\alpha_{\text{NO}_2/\text{NO}}$  relative to the  $\delta^{15}\text{N-NO}_x$  (Figure 3).

In Figure 3a, the  $\delta^{15}\text{N-NO}_2$  diurnal profile is derived from hourly measurements of NO,  $\text{NO}_2$ , and temperature at Indianapolis, IN, USA (39.8151°N, and –86.1118°W) from 13 September 2015 to 19 September 2015 [Indiana Department of Environmental Management, 2015]. The  $\delta^{15}\text{N-NO}_2$  has a diurnal cycle (Figure 3a) with a daily maximum of  $12.9 \pm 2.4\text{‰}$ , which typically occurs between 8:00 A.M. and 1:00 P.M. when local  $f_{\text{NO}_2}$  values are the lowest. The  $f_{\text{NO}_2}$  is lowest during this period due to the emission of NO from transportation-related combustion sources, typical of urban areas [Gao, 2007], as well as the photolysis of  $\text{NO}_2$  during the daytime [Leighton, 1961]. Under these conditions, the  $\text{NO}_x$  isotope exchange has a significant influence on the partitioning of  $\delta^{15}\text{N}$  between NO and  $\text{NO}_2$ , and this is shown in Figure 3a with a dotted line. During

the evening and nighttime, however,  $f_{\text{NO}_2}$  approaches 1 as all NO is oxidized by  $\text{O}_3$  into  $\text{NO}_2$ , but NO is not reformed due to the absence of  $\text{NO}_2$  photolysis [Leighton, 1961]. Under these conditions,  $\delta^{15}\text{N-NO}_2$  approaches 0‰ indicating that  $\delta^{15}\text{N-NO}_2$  is approximately equal to the  $\delta^{15}\text{N-NO}_x$ , and this is shown in Figure 3b with a dashed line.

Predicted seasonal changes in  $\delta^{15}\text{N-NO}_2$  (Figure 3b) were derived from hourly measurements of NO,  $\text{NO}_2$ , and temperature recorded at Chula Vista, CA, USA (32.6278°N and 117.0481°W) from 1 January 2007 to 31 December 2007 [California Environmental Protection Agency, 2015]. There is relatively large scatter in  $\delta^{15}\text{N-NO}_2$  and  $f_{\text{NO}_2}$  throughout the year (Figure 3b), and this is related to the diurnal cycle that both  $\delta^{15}\text{N-NO}_2$  and  $f_{\text{NO}_2}$  exhibit. The 100 h moving average, however, shows that there may be slight seasonal variations in  $\delta^{15}\text{N-NO}_2$  (Figure 3b). The model predicts that during the winter (December–February),  $\delta^{15}\text{N-NO}_2$  would have the highest average 100 h moving average of 10.3‰, compared to the other seasons that have similar average 100 h moving averages of 7.36‰, 7.79‰, and 7.83‰ for spring (March–May), summer (June–August), and fall (September–November), respectively. The observed slightly higher  $\delta^{15}\text{N-NO}_2$  100 h moving average for winter is related to both the seasonal changes in  $f_{\text{NO}_2}$  and in temperatures. Both of these parameters will result in higher  $\delta^{15}\text{N-NO}_2$  values in winter relative to the other seasons, as N isotopic exchange is temperature dependent and is greater at lower temperatures and a lower  $f_{\text{NO}_2}$  will result in more  $^{15}\text{N}$  enrichment in  $\text{NO}_2$ . At Chula Vista, there is relatively small fluctuations in seasonal temperatures and  $f_{\text{NO}_2}$  (Figure 3b), however, at sites with larger variations in these parameters, it is expected that there will be a more pronounced seasonal cycling of  $\delta^{15}\text{N-NO}_2$ .

The simple case in which NO and  $\text{NO}_2$  always exist in N isotopic equilibrium is competing with isotope fractionation factors and lifetimes associated with the Leighton cycle [Freyer *et al.*, 1993]:

$$\tau_{\text{NO}+\text{O}_3} = \frac{1}{k_{\text{NO}+\text{O}_3}[\text{O}_3]} \quad (\text{R5})$$

$$\tau_{\text{NO-exchange}} = \frac{1}{k_{^{15}\text{N}\text{NO} + ^{14}\text{N}\text{NO}_2}[\text{NO}_2]} \quad (\text{R6})$$

$$\tau_{\text{NO}_2\text{-exchange}} = \frac{1}{k_{^{15}\text{N}\text{NO} + ^{14}\text{N}\text{NO}_2}[\text{NO}]} \quad (\text{R7})$$

$$\tau_{\text{NO}_2+\text{hv}} = \frac{1}{j_{\text{NO}_2}}. \quad (\text{R8})$$

Here  $\tau$  is lifetime (e-folding time) of each reaction,  $k$  are the rate constants ( $\text{NO} + \text{O}_3 = 1.73 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  [Atkinson *et al.*, 2004] and  $\text{NO}_x$  isotope exchange =  $8.14 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  [Sharma *et al.*, 1970]), and  $j$  is photolysis rate constant  $\sim 5 \times 10^{-3} \text{ s}^{-1}$ , which depends upon solar zenith angle [Parrish *et al.*, 1983]. Using these constants and concentrations of 5 ppb of NO, 5 ppb  $\text{NO}_2$ , and 20 ppb of  $\text{O}_3$ ,  $\tau_{\text{NO}+\text{O}_3}$ ,  $\tau_{\text{NO-exchange}}$ ,  $\tau_{\text{NO}_2\text{-exchange}}$ , and  $\tau_{\text{NO}_2+\text{hv}}$  are calculated to be 1.9, 1.6, 1.6, and 1.9 min respectively. Under these conditions, the lifetimes of the Leighton cycle reactions and  $\text{NO}_x$  exchange are comparable, therefore, the associated N fractionation factor between NO and  $\text{NO}_2$  will be a mixture of these processes. If one of the lifetimes (R5–R8) is an order of magnitude shorter relative to the others, the associated N fractionation factor between NO and  $\text{NO}_2$  will be closer to the shorter lifetime's N fractionation factor. For example, when NO and  $\text{NO}_2$  concentrations are increased to 80 ppb,  $\tau_{\text{NO-exchange}}$  and  $\tau_{\text{NO}_2\text{-exchange}}$  decreases to 0.1 min and the NO and  $\text{NO}_2$   $\delta^{15}\text{N}$  values will more closely match the  $\text{NO}_x$  exchange fractionation factor. Such conditions may exist downwind of smoke stack plumes during the daytime. Conversely, during high  $\text{O}_3$  (20 ppb) and low  $\text{NO}_x$  (100 ppt), such as the open ocean,  $\tau_{\text{NO-exchange}}$  and  $\tau_{\text{NO}_2\text{-exchange}}$  are 100 times slower than photolysis and  $\text{O}_3$  oxidation and thus is unlikely to be relevant. The N fractionation factors associated with the  $\text{NO} + \text{O}_3$  reaction and  $\text{NO}_2$  photolysis has yet to be determined but will be the subject of ongoing research. During the night when photolysis ceases and nearly all  $\text{NO}_x$  exists as  $\text{NO}_2$ , the  $\delta^{15}\text{N}$  of  $\text{NO}_2$  will reflect the  $\delta^{15}\text{N}$  of the emitted  $\text{NO}_x$  in that region. Overall, the N fractionation between NO and  $\text{NO}_2$  is complicated, but future research in the kinetic modeling of Leighton/ $\text{NO}_x$  exchanging process will help elucidate the importance of the various N fractionation factors under varying conditions.

The  $\delta^{15}\text{N}$  value of atmospheric nitrate formed from the  $\text{NO}_x$  will depend not only on the  $\delta^{15}\text{N}$  value of the  $\text{NO}_2$  but also kinetic and equilibrium isotope effects occurring during its oxidation into  $\text{NO}_3^-$ . During the daytime, atmospheric nitrate is primarily formed through the reaction  $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3$ . Therefore,  $\delta^{15}\text{N}$  value of atmospheric nitrate formed during the day will be a complex function of the  $\delta^{15}\text{N}$  of the emitted  $\text{NO}_x$ , the  $\text{NO}_x$  equilibrium/Leighton reaction fractionation factors, and the fractionation factor associated with the  $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$  reaction, which is currently unknown.

During the nighttime, atmospheric nitrate is primarily formed through the formation of  $\text{N}_2\text{O}_5$  and its subsequent hydrolysis.  $\text{N}_2\text{O}_5$  exists in equilibrium with  $\text{NO}_2$  and nitrate radical ( $\text{NO}_3$ ):



Since nighttime  $\delta^{15}\text{N}\text{-NO}_2$  should be reflective of the  $\delta^{15}\text{N}$  of the  $\text{NO}_x$  sources, the  $\text{N}_2\text{O}_5$   $\delta^{15}\text{N}$  value will depend on the emitted  $\text{NO}_x$  sources and the isotope exchange associated with the  $\text{N}_2\text{O}_5$  equilibrium ((R9)). At N isotopic equilibrium,  $\text{N}_2\text{O}_5$  is predicted to be 26.9‰ and 31.1‰ enriched in  $\delta^{15}\text{N}$  relative to  $\text{NO}_2$  and  $\text{NO}_3$  at 298 K [Walters and Michalski, 2015]. Therefore,  $\delta^{15}\text{N}$  of atmospheric nitrate formed in the absence of sunlight should be  $^{15}\text{N}$  enriched relative to the  $\text{NO}_x$ , which is a possible explanation for the observed high  $\delta^{15}\text{N}$  values of atmospheric nitrate during winter months when there is less sunlight [Freyer, 1978, 1991; Elliott et al., 2007, 2009; Riha, 2013] in addition to predicted seasonal changes in  $\delta^{15}\text{N}\text{-NO}_x$  [Walters et al., 2015].

#### 4. Conclusions

Previously, there has been disagreement between experimental measurements and theoretical calculations of the N isotope exchange between NO and  $\text{NO}_2$ . In this study, we measured this exchange process to have an  $\alpha_{\text{NO}_2/\text{NO}}$  of 1.0403 (278 K), 1.0356 (297 K), and 1.0336 (310 K). These values are within experimental error of the values calculated using a modified version of the Bigeleisen-Mayer equation corrected for accurate ZPEs by including anharmonicity. Temperature-dependent fractionation factors were calculated and used to model seasonal changes in  $\delta^{15}\text{N}\text{-NO}_2$ . The model predicts that  $\delta^{15}\text{N}\text{-NO}_2$  values will exhibit a pronounced diurnal oscillation and have seasonal variations that depend upon  $f_{\text{NO}_2}$  and ambient temperature. If  $\delta^{15}\text{N}$  of atmospheric nitrate is linked to the  $\delta^{15}\text{N}\text{-NO}_2$ , then our model predicts that (1)  $\delta^{15}\text{N}$  diurnal variations would be found in atmospheric nitrate, (2) elevated winter  $\delta^{15}\text{N}$  should be observed in  $\delta^{15}\text{N}$  of atmospheric nitrate due to N isotope exchange between NO and  $\text{NO}_2$ , (3) relatively large seasonal variations in  $\delta^{15}\text{N}$  of atmospheric nitrate will be observed in regions with relatively large seasonal changes in temperature and  $f_{\text{NO}_2}$ , and (4) there will be diurnal variation in  $\delta^{15}\text{N}\text{-NO}_x$  values, with nighttime values reflecting the local/regional  $\text{NO}_x$  sources. Future simultaneous  $\delta^{15}\text{N}$  measurements of atmospheric nitrate and  $\text{NO}_2$  will be useful in determining the correlation between the two. Additionally, other N isotope effects involving the oxidation of  $\text{NO}_x$  to atmospheric nitrate, the dry deposition of NO and  $\text{NO}_2$ , and the photolysis of  $\text{NO}_2$  still need to be considered and will be the subject for future research.

#### Acknowledgments

W.W.W. was a National Science Foundation Graduate Research Fellow (grant DGE-1333468) during the course of the study. We would like to thank the Purdue Climate Change Research Center (PCCRC) graduate fellowship program for supporting this work (PCCRC paper 1554). D.S.S. acknowledges support from the Purdue Center for Environment undergraduate research award and the Purdue Chemistry Summer Research Stipend/Margerum Award. The data supporting the conclusions can be found in the supporting information. We would like to thank two anonymous reviewers for their helpful comments.

#### References

- Ali, Z., C. L. P. Thomas, and J. F. Alder (1989), Denuder tubes for sampling of gaseous species. A review, *Analyst*, 114(7), 759–769, doi:10.1039/AN9891400759.
- Ammann, M., R. Siegwolf, F. Pichlmayer, M. Suter, M. Saurer, and C. Brunold (1999), Estimating the uptake of traffic-derived  $\text{NO}_2$  from  $^{15}\text{N}$  abundance in Norway spruce needles, *Oecologia*, 118(2), 124–131, doi:10.1007/s004420050710.
- Atkinson, R., D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, and J. Troe (2004), Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I—gas phase reactions of  $\text{O}_x$ ,  $\text{HO}_x$ ,  $\text{NO}_x$  and  $\text{SO}_x$  species, *Atmos. Chem. Phys.*, 4(6), 1461–1738.
- Begun, G. M., and C. E. Melton (1956), Nitrogen isotopic fractionation between NO and  $\text{NO}_2$  and mass discrimination in mass analysis of  $\text{NO}_2$ , *J. Chem. Phys.*, 25(6), 1292–1293, doi:10.1063/1.1743215.
- Begun, G. M., and W. H. Fletcher (1960), Partition function ratios for molecules containing nitrogen isotopes, *J. Chem. Phys.*, 33(4), 1083–1085.
- Bigeleisen, J., and M. G. Mayer (1947), Calculation of equilibrium constants for isotopic exchange reactions, *J. Chem. Phys.*, 15(5), 261–267, doi:10.1063/1.1746492.
- Blank, R. E., and C. D. Hause (1970), Molecular constants for the (3, 0, 1) band of  $\text{NO}_2$ , *J. Mol. Spectrosc.*, 34(3), 478–486, doi:10.1016/0022-2852(70)90028-7.
- California Environmental Protection Agency (2015), Air quality data (PST) query tool. [Available at <http://www.arb.ca.gov/aqmis2/aqselect.php?tab=hourly>, Accessed 23 Sept.]
- Crutzen, P. J. (1973), *Gas-Phase Nitrogen and Methane Chemistry in the Atmosphere*, D. Reidel Comp., Dordrecht, Holland.



- Crutzen, P. J. (1979), The role of NO and NO<sub>2</sub> in the chemistry of the troposphere and stratosphere, *Annu. Rev. Earth Planet. Sci.*, *7*, 443–472.
- Elliott, E. M., C. Kendall, S. D. Wankel, D. A. Burns, E. W. Boyer, K. Harlin, D. J. Bain, and T. J. Butler (2007), Nitrogen isotopes as indicators of NO<sub>x</sub> source contributions to atmospheric nitrate deposition across the midwestern and northeastern United States, *Environ. Sci. Technol.*, *41*(22), 7661–7667.
- Elliott, E. M., C. Kendall, E. W. Boyer, D. A. Burns, G. G. Lear, H. E. Golden, K. Harlin, A. Bytnerowicz, T. J. Butler, and R. Glatz (2009), Dual nitrate isotopes in dry deposition: Utility for partitioning NO<sub>x</sub> source contributions to landscape nitrogen deposition, *J. Geophys. Res.*, *114*, G04020, doi:10.1029/2008JG000889.
- Freyer, H. D. (1978), Seasonal trends of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> nitrogen isotope composition in rain collected at Jülich, Germany, *Tellus*, *30*(1), 83–92.
- Freyer, H. D. (1991), Seasonal variation of <sup>15</sup>N/<sup>14</sup>N ratios in atmospheric nitrate species, *Tellus B*, *43*(1), 30–44.
- Freyer, H. D., D. Kley, A. Volz-Thomas, and K. Kobel (1993), On the interaction of isotopic exchange processes with photochemical reactions in atmospheric oxides of nitrogen, *J. Geophys. Res.*, *98*(D8), 14,791–14,796.
- Gao, H. O. (2007), Day of week effects on diurnal ozone/NO<sub>x</sub> cycles and transportation emissions in Southern California, *Transp. Res. Part D: Transp. Environ.*, *12*(4), 292–305.
- Heaton, T. H. E. (1987), <sup>15</sup>N/<sup>14</sup>N ratios of nitrate and ammonium in rain at Pretoria, South Africa, *Atmos. Environ.*, *21*(4), 843–852.
- Henry, A., M. F. Le Moal, P. Cardinet, and A. Valentin (1978), Overtone bands of <sup>14</sup>N<sup>16</sup>O and determination of molecular constants, *J. Mol. Spectrosc.*, *70*(1), 18–26, doi:10.1016/0022-2852(78)90004-8.
- Hurtmans, D., M. Herman, and J. Vander Auwera (1993), Integrated band intensities in N<sub>2</sub>O<sub>4</sub> in the infrared range, *J. Quant. Spectros. Radiat. Transfer*, *50*(6), 595–602, doi:10.1016/0022-4073(93)90027-F.
- Indiana Department of Environmental Management (2015), Indpls-Washington Park Data by site by date. [Available at [http://idem.tx.sutnon.com/cgi-bin/daily\\_summary.pl?cams=42](http://idem.tx.sutnon.com/cgi-bin/daily_summary.pl?cams=42), Accessed 23 Sept.]
- Leifer, E. (1940), The exchange of oxygen between NO and NO<sub>2</sub>, *J. Chem. Phys.*, *8*(4), 301–303, doi:10.1063/1.1750652.
- Leighton, P. (1961), *Photochemistry of Air Pollution*, Academic, New York.
- Li, D., and X. Wang (2008), Nitrogen isotopic signature of soil-released nitric oxide (NO) after fertilizer application, *Atmos. Environ.*, *42*(19), 4747–4754, doi:10.1016/j.atmosenv.2008.01.042.
- Liu, Q., J. A. Tossell, and Y. Liu (2010), On the proper use of the Bigeleisen–Mayer equation and corrections to it in the calculation of isotopic fractionation equilibrium constants, *Geochim. Cosmochim. Acta*, *74*(24), 6965–6983, doi:10.1016/j.gca.2010.09.014.
- Logan, J. A. (1983), Nitrogen oxides in the troposphere: Global and regional budgets, *J. Geophys. Res.*, *88*(C15), 10,785–10,807, doi:10.1029/JC088iC15p10785.
- McIlvin, M. R., and M. A. Altabet (2005), Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater, *Anal. Chem.*, *77*(17), 5589–5595, doi:10.1021/ac050528s.
- Michalski, G., R. Jost, D. Sugny, M. Joyeux, and M. Thiemens (2004), Dissociation energies of six NO<sub>2</sub> isotopologues by laser induced fluorescence spectroscopy and zero point energy of some triatomic molecules, *J. Chem. Phys.*, *121*(15), 7153–7161, doi:10.1063/1.1792233.
- Monse, E. U., W. Spindel, and M. J. Stern (1969), Analysis of isotope-effect calculations illustrated with exchange equilibria among oxy-nitrogen compounds, *ACS Adv. Chem. Ser.*, *89*, 148–184.
- Olman, M. D., M. D. McNelis, and C. D. Hause (1964), Molecular constants of nitric oxide from the near infrared spectrum, *J. Mol. Spectrosc.*, *14*(1–4), 62–78, doi:10.1016/0022-2852(64)90100-6.
- Parrish, D. D., P. C. Murphy, D. L. Albritton, and F. C. Fehsenfeld (1983), The measurement of the photodissociation rate of NO<sub>2</sub> in the atmosphere, *Atmos. Environ.*, *17*(7), 1365–1379.
- Richtel, P., Y. Bottinga, and M. Janoy (1977), A review of hydrogen, carbon, nitrogen, oxygen, sulphur, and chlorine stable isotope enrichment among gaseous molecules, *Annu. Rev. Earth Planet. Sci.*, *5*, 65–110.
- Riha, K. M. (2013), *The Use of Stable Isotopes to Constrain the Nitrogen Cycle*, PhD Dissertation, Purdue Univ.
- Rinsland, C. P., R. E. Boughner, J. C. Larsen, G. M. Stokes, and J. W. Brault (1984), Diurnal variations of atmospheric nitric oxide: Ground-based infrared spectroscopic measurements and their interpretation with time-dependent photochemical model calculations, *J. Geophys. Res.*, *89*(D6), 9613–9622, doi:10.1029/JD089iD06p09613.
- Ryabenko, E., M. A. Altabet, and D. W. R. Wallace (2009), Effect of chloride on the chemical conversion of nitrate to nitrous oxide for δ<sup>15</sup>N analysis, *Limnol. Oceanogr. Methods*, *7*(7), 545–552, doi:10.4319/lom.2009.7.545.
- Savarino, J., S. Morin, J. Erbland, F. Grannec, M. D. Patey, W. Vicars, B. Alexander, and E. P. Achterberg (2013), Isotopic composition of atmospheric nitrate in a tropical marine boundary layer, *Proc. Natl. Acad. Sci. U.S.A.*, *110*(44), 17,668–17,673, doi:10.1073/pnas.1216639110.
- Seinfeld, J. H., and S. N. Pandis (2006), *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley, New York.
- Sharma, H. D., R. E. Jervis, and K. Y. Wong (1970), Isotopic exchange reactions in nitrogen oxides, *J. Phys. Chem.*, *74*(4), 923–933, doi:10.1021/j100699a044.
- Teffo, J. L., A. Henry, P. Cardinet, and A. Valentin (1980), Determination of molecular constants of nitric oxide from (1–0), (2–0), (3–0) bands of the <sup>15</sup>N<sup>16</sup>O and <sup>15</sup>N<sup>18</sup>O isotopic species, *J. Mol. Spectrosc.*, *82*(2), 348–363, doi:10.1016/0022-2852(80)90120-4.
- Urey, H. C. (1947), The thermodynamic properties of isotopic substances, *J. Chem. Soc.*, *7*, 562–581.
- Verhoeve, F. H., and F. Daniels (1931), The dissociation constants of nitrogen tetroxide and of nitrogen trioxide, *J. Am. Chem. Soc.*, *53*(4), 1250–1263, doi:10.1021/ja01355a009.
- Walters, W. W., and G. Michalski (2015), Theoretical calculation of nitrogen isotope equilibrium exchange fractionation factors for various NO<sub>y</sub> molecules, *Geochim. Cosmochim. Acta*, *164*, 284–297, doi:10.1016/j.gca.2015.05.029.
- Walters, W. W., B. D. Tharp, H. Fang, B. J. Kozak, and G. Michalski (2015), Nitrogen isotope composition of thermally produced NO<sub>x</sub> from various fossil-fuel combustion sources, *Environ. Sci. Technol.*, *49*(19), 11,363–11,371, doi:10.1021/acs.est.5b02769.
- Williams, E. L., and D. Grosjean (1990), Removal of atmospheric oxidants with annular denuders, *Environ. Sci. Technol.*, *24*(6), 811–814, doi:10.1021/es00076a002.
- Wilson, E. B., J. C. Decius, and P. C. Cross (1955), *Molecular Vibrations*, McGraw-Hill, New York.