Quantifying the nitrogen equilibrium and photochemistry-induced isotopic effects between NO and NO₂

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Abstract. The nitrogen isotopic fractionations between NO and NO₂ play a significant role in determining the nitrogen isotopic compositions (δ¹⁵N) of atmospheric NO₂ and nitrate. This isotopic fractionation is controlled by a combination of equilibrium isotopic effect (EIE) and Leighton Cycle induced isotopic effect (LCIE), which are poorly constrained. We quantified this isotopic fractionation process by 1) measuring the isotopic fractionation factors of EIE and LCIE in a 10 m³ atmospheric simulation chamber and 2) mathematically calculating the relative importance of EIE and LCIE. Our results showed the enrichment factors of EIE and LCIE are 1.0275±0.0012, and 0.990±0.005, respectively, at room temperature. We find that EIE is the dominate factor when NOₓ > 20 nmol mol⁻¹, and LCIE is more important at low NOₓ concentrations (<1 nmol mol⁻¹) and high rates of photolysis of NO₂ (j(NO₂)). Our study provides a mathematical solution to calculate the NO-NO₂ isotopic fractionation at any given condition.
1. Introduction

The variation in the nitrogen isotopic composition ($\delta^{15}N$) of NO$_2$ and nitrate is an important tool in understanding the sources and chemistry of atmospheric NO$_x$ (NO+NO$_2$). Atmospheric NO$_2$($g$), nitrate aerosols, and nitrate ion in the precipitation imprint the $\delta^{15}N$ of their sources (Elliott et al., 2009; Kendall et al., 2007) thus many studies have used the $\delta^{15}N$ values of atmospheric NO$_2$($g$) or nitrate to investigate NO$_x$ sources (Chang et al., 2018; Felix et al., 2012; Felix & Elliott, 2014; Gobel et al., 2013; Hastings et al., 2004, 2009; Morin et al., 2009; Park et al., 2018; Walters et al., 2015, 2018). However, there remain questions about how isotopic fractionations occurring during photochemical recycling of NO$_x$ and its conversion into NO$_y$ (NO$_3$, N$_2$O$_5$, HONO, etc.) and nitrate alter the $\delta^{15}N$ values of NO$_x$ (Chang et al., 2018; Freyer, 1991; Hastings et al., 2004; Jarvis et al., 2008; Michalski et al., 2005; Morin et al., 2009; Zong et al., 2017). Isotopic fractionations occur in most, if not all, NO$_x$ and NO$_y$ reactions. However, most isotopic fractionation factors related to NO$_x$ and NO$_y$ chemistry are still unknown. In addition, since the atmospheric chemistry of NO$_x$ varies significantly in different environments (e.g., polluted vs. pristine, night vs. noon), the isotopic fractionations associated with the chemistry are also likely to vary under different environments. These uncertainties could potentially bias conclusions reached on NO$_x$ source apportionment using nitrogen isotopes. Therefore, a better quantification of these isotopic fractionations is needed. The isotopic fractionations between NO and NO$_2$ have been suggested to be the dominant factor in determining the $\delta^{15}N$ of NO$_2$ and ultimately nitrate (Freyer, 1991; Freyer et al., 1993; Savarino et al., 2013; Walters et al., 2016), therefore understanding the isotopic fractionations between NO and NO$_2$ could improve our understanding on the isotopes of atmospheric NO$_2$ and nitrate.
In general, there are three types of isotope fractionation effects associated with NO\textsubscript{x} chemistry: 1) the equilibrium isotopic effect (EIE), i.e., isotopic exchange between two compounds without forming new molecules (Freyer et al., 1993; Walters et al., 2016), for nitrogen isotopes in the NO\textsubscript{x} system this is the \textsuperscript{15}NO + \textsuperscript{14}NO\textsubscript{2} ↔ \textsuperscript{14}NO + \textsuperscript{15}NO\textsubscript{2} exchange reaction; 2) the kinetic isotopic effect (KIE) associated with difference in isotopologue rate coefficients during unidirectional reactions (Bigeleisen & Wolfsberg, 1957), in the NO\textsubscript{x} system these could be manifest in the oxidation of NO into NO\textsubscript{2} by O\textsubscript{3}/HO\textsubscript{2}/RO\textsubscript{2}; 3) the photochemical isotopic fractionation effect (PHIFE, Michalski et al., 2004; Miller & Yung, 2000), which for NO\textsubscript{x} is the isotopic fractionation associated with NO\textsubscript{2} photolysis. All three fractionations impact the \textsuperscript{15}N value of NO\textsubscript{2} and consequently nitrate but the relative importance of each may vary. Additionally, in the NO\textsubscript{y} cycle, EIE (isotopic exchange between NO\textsubscript{2}, NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5}), KIE (formation of NO\textsubscript{3}, N\textsubscript{2}O\textsubscript{5} and nitrate) and PHIFE (photolysis of NO\textsubscript{3}, N\textsubscript{2}O\textsubscript{5}, HONO and sometimes nitrate) may also exist and be relevant for the \textsuperscript{15}N of HNO\textsubscript{3} and HONO, but these will not be discussed in this work.

The isotopic fractionation factors of EIE, KIE and PHIFE in the NO\textsubscript{x} cycle still have significant uncertainties. Discrepancies in the EIE for \textsuperscript{15}NO + \textsuperscript{14}NO\textsubscript{2} ↔ \textsuperscript{14}NO + \textsuperscript{15}NO\textsubscript{2} have been noted in several studies. Theoretical calculations predict fractionation factors (\(\alpha\)) ranging from 1.035 to 1.042 at room temperature (Begun & Fletcher, 1960; Monse et al., 1969; Walters & Michalski, 2015). In contrast two separate experiments measured slightly different fractionation factors of 1.028±0.002 (Begun & Melton, 1956) and 1.0356±0.001 (Walters et al., 2016). A concern in both experiments is that they were conducted in chambers with extremely high NO\textsubscript{x} concentrations (hundreds of \(\mu\)mol mol\textsuperscript{-1}) that were significantly higher than typical ambient atmospheric NO\textsubscript{x} levels (usually <100 nmol mol\textsuperscript{-1}). Whether the isotopic fractionation factors determined by these experiments are applicable in the ambient environment is uncertain. KIE and PHIFE have been
rarely studied theoretically or experimentally and were often overlooked. Freyer et al. (1993) suggested that the NO\textsubscript{x} photochemical cycle (KIE and PHIFE) tends to diminish the equilibrium isotopic fractionation (EIE) between NO and NO\textsubscript{2} if it assumed that the isotopic fractionation factors of KIE and PHIFE are both 1. Alternatively, Freyer et al. (1993) estimated the isotopic fractionation factor between NO and NO\textsubscript{2} at Julich, Germany over a 1-year period which averaged at 1.018±0.001 and suggested that this fractionation factor was a combined effect of EIE, KIE and PHIFE. Even if this approach were valid, applying this single fractionation factor elsewhere, where NO\textsubscript{x}, O\textsubscript{3} concentrations and actinic fluxes are likely different, would be tenuous given that these factors may influence the relative importance of EIE, KIE and PHIFE (Hastings et al., 2004; Walters et al., 2016). Therefore, to quantify the overall isotopic fractionations between NO and NO\textsubscript{2} at any given condition, it is crucial to know 1) isotopic fractionation factors of EIE, KIE and PHIFE individually and 2) the relative importance of each factor in various conditions.

In this work, we aim to quantify the nitrogen isotopic fractionation between NO and NO\textsubscript{2} at photochemical equilibrium. First, we measure the isotopic fractionations between NO and NO\textsubscript{2} in an atmospheric simulation chamber at atmospheric relevant NO\textsubscript{x} levels. Then, we provide mathematical solutions to assess the impact of NO\textsubscript{x} level and NO\textsubscript{2} photolysis rate (j(NO\textsubscript{2})) to the relative importance of EIE, KIE and PHIFE. Subsequently we use the solutions and chamber measurements to calculate the isotopic fractionation factors of EIE, KIE and PHIFE. Last, using the calculated fractionation factors and the equations, we model the NO-NO\textsubscript{2} isotopic fractionations at several sites to illustrate the behavior of NO\textsubscript{x} nitrogen isotopes in the ambient environment.

2. Methods
The experiments were conducted using a 10 m³ Atmospheric Simulation Chamber at the National Center for Atmospheric Research (see descriptions in supplementary material and Zhang et al. (2018)). A set of mass flow controllers was used to inject NO and O₃ into the chamber: NO was injected at 1 L min⁻¹ from an in-house concentrated NO cylinder (133.16 µmol mol⁻¹ NO in ultra-pure N₂), and O₃ was generated by flowing 5 L min⁻¹ zero-air through a flow tube equipped with a Pen-Ray lamp (UVP LLC., CA) into the chamber. The wall loss rate of NO₂ was tested and found to be negligible (see supplementary material). In each experiment, the actual amounts of NO and O₃ injected were calculated using measured NOₓ and O₃ concentrations after steady state was reached (usually within 1 h).

Two sets of experiments were conducted to separately investigate the EIE, KIE and PHIFE. The first set of experiments was conducted in the dark. In each experiment, a range of NO and O₃ ([O₃]<[NO]) was injected into the chamber to produce NO-NO₂ mixtures. The N isotopes of these mixtures were used to investigate the EIE between NO and NO₂. The second set of experiments was conducted under irradiation of UV lights. Under such conditions, NO, NO₂ and O₃ reached photochemical steady state, which revealed the combined isotopic effects of EIE, KIE and PHIFE.

In addition, the δ¹⁵N value of source NO was measured throughout the experiments. For each test, a certain amount of O₃ was injected into the chamber, then approximately the same amount of NO was injected into the chamber to ensure all the NOₓ was in the form of NO₂ with little O₃ (<3 nmol mol⁻¹) remaining in the chamber such that the O₃+NO₂ reaction was negligible, the δ¹⁵N value of NO₂ therefore represented the δ¹⁵N of source NO.

During each experiment, once the concentrations of NO, NO₂ and O₃ reached steady state, NO₂ was collected from the chamber onto a honeycomb denuder tube as NO₂⁺ while NO was inert to the chemicals on the denuder tubes. The NO₂ collection efficiency of a single honeycomb
denuder tube was tested to be nearly 100% (see supplementary material). Each denuder tube was then rinsed thoroughly with 10 ml deionized water into a clean polypropylene centrifuge tube and stored frozen until isotopic analysis. Isotopic analysis was conducted at Purdue Stable Isotope Laboratory. For each sample, approximately 50 nmol of NO\textsubscript{2} was mixed with 2 M sodium azide solution in acetic acid buffer in an air-tight glass vial, then shaken overnight to completely reduce all the NO\textsubscript{2} to N\textsubscript{2}O\textsubscript{(g)} (Casciotti & McIlvin, 2007; McIlvin & Altabet, 2005). The product N\textsubscript{2}O was directed into a Finnigan GasBench equipped with cryo-trap then the $\delta^{15}$N of the N\textsubscript{2}O was measured by a Delta-V Isotope Ratios Mass Spectrometer (IRMS). The overall analytical uncertainty for $\delta^{15}$N analysis was ±0.5 ‰ (1σ) based on replicate analysis of in house NO\textsubscript{2} standards.

3. Results and Discussions

3.1. Equilibrium Isotopic Fractionation between NO and NO\textsubscript{2}

The equilibrium isotopic fractionation factor $\alpha$(NO\textsubscript{2}-NO) is the $^{15}$N enrichment in NO\textsubscript{2} relative to NO, and is expressed as the difference in rate constants between the two reactions:

\[ ^{15}\text{NO} + ^{14}\text{NO} \rightarrow ^{15}\text{NO} + ^{14}\text{NO} \]  
R1, rate constant=$k_1$

\[ ^{15}\text{NO} + ^{14}\text{NO}_2 \rightarrow ^{15}\text{NO}_2 + ^{14}\text{NO} \]  
R2, rate constant=$k_1 \times \alpha$(NO\textsubscript{2}-NO)

where $k_1$ is the rate constant of the isotopic exchange, which was previously determined to be $8.14 \times 10^{-14}$ cm\textsuperscript{3} s\textsuperscript{-1} (Sharma et al., 1970). The reaction time for NO-NO\textsubscript{2} to reach isotopic equilibrium was estimated using a simple box model containing N isotopic information (see supplementary information). At the NO\textsubscript{x} level during the chamber experiments (7.7-62.4 nmol mol\textsuperscript{-1}), the isotopic equilibrium was reached within 15 min, and the sample collection usually
started 1 hour after NO\(_x\) was well mixed in the chamber. The isotope equilibrium fractionation factor is then calculated to be:

\[
\alpha(\text{NO}_2 - \text{NO}) = \frac{[^{15}\text{NO}_2] \times [^{14}\text{NO}]}{[^{14}\text{NO}_2] \times [^{15}\text{NO}]} = \frac{\text{R(\text{NO}_2)}}{\text{R(\text{NO})}} \tag{1}
\]

where R(\text{NO}, \text{NO}_2) are the \(^{15}\text{N}/^{14}\text{N} \) ratios of NO\(_1\), \(_2\). As \(\delta(\text{NO})=(\text{R(\text{NO})}/\text{R(\text{reference})}) - 1 \times 1000 \%
\)

and \(\delta(\text{NO}_2)=(\text{R(\text{NO}_2})/\text{R(\text{reference})}) - 1 \times 1000 \%
\) (hereafter, the \(\delta^{15}\text{N} \) values of NO, NO\(_2\) and NO\(_x\) are referred as \(\delta(\text{NO})\), \(\delta(\text{NO}_2)\) and \(\delta(\text{NO}_x)\), respectively, Eq. (1) leads to:

\[
\delta(\text{NO}_2) - \delta(\text{NO}) = (\alpha(\text{NO}_2 - \text{NO}) - 1) \times 1000 \% \times (1 + \delta(\text{NO}))
\]

\[
= \varepsilon(\text{NO}_2 - \text{NO}) \times (1 + \delta(\text{NO})) \tag{2}
\]

where \(\varepsilon(\text{NO}_2-\text{NO})\) is the isotope enrichment factor (in permil (%), Hoefs, 2009). Combining Eq. (2) with the NO\(_x\) isotopic mass balance (\(\delta(\text{NO}_x)=f(\text{NO}_2)\times\delta(\text{NO}_2)+1-f(\text{NO}_2))\times\delta(\text{NO}),
\)

\[
f(\text{NO}_2)=\frac{[\text{NO}_2]/([\text{NO}]+[\text{NO}_2])}
\]

yields:

\[
\delta(\text{NO}_2) - \delta(\text{NO}_x) = \varepsilon(\text{NO}_2 - \text{NO}) \times (1 + \varepsilon(\text{NO}_2 - \text{NO})) \times (1 + \delta(\text{NO}_x)) \times (1 - f(\text{NO}_2)) \tag{3}
\]

In which \(\delta(\text{NO}_x)\) equals to the \(\delta^{15}\text{N} \) of source NO, and \(f(\text{NO}_2)\) is the molar fraction of NO\(_2\). Three calibration experiments that measured \(\delta(\text{NO}_x)\) before, during and after all the experiments showed consistent \(\delta(\text{NO}_x)\) values of -58.7±0.8 % (n = 3), indicating \(\delta(\text{NO}_x)\) remained unchanged throughout the experiments. Thus, the \(\delta(\text{NO}_x)\) can be treated as a constant in Eq. (3), and the slope of a linear regression of \((\delta(\text{NO}_2)-\delta(\text{NO}_x))/(1+\delta(\text{NO}_2))) \) versus \(1-f(\text{NO}_2))\) represents \(\varepsilon(\text{NO}_2-\text{NO})/(1+\varepsilon(\text{NO}_2-\text{NO})).
\]

The plot of \((\delta(\text{NO}_2)-\delta(\text{NO}_x))/(1+\delta(\text{NO}_2))) \) as a function of \(1-f(\text{NO}_2))\) values from five experiments yields a slope of +26.8±1.2 % (Fig. 1A) therefore an \(\varepsilon(\text{NO}_2-\text{NO})\) of 27.5±1.2 % at room temperature. This fractionation factor was comparable to previously measured values with some differences. Our result agrees well with the \(\alpha(\text{NO}_2-\text{NO})\) value of 1.028±0.002 obtained by
Begun and Melton (1956) at room temperature. However, Walters et al., (2016) determined the
α(NO2-NO) values of NO-NO2 exchange in a 1-liter reaction vessel, which showed a slightly
higher α(NO2-NO) value of 1.035. This discrepancy likely originates from rapid heterogeneous
reactions on the wall of the reaction vessel at high NOx concentrations in Walters et al.
(2016). Walters et al. (2016) used a vacuum line and Pyrex reaction vessel, which are known to
absorb water (Do Remus et al., 1983; Takei et al., 1997) that can react with NO2 forming HONO,
HNO3 and other species. Additionally, previous studies have suggested that glass walls could
enhance the formation rate of N2O4 by over an order of magnitude (Barney & Finlayson-Pitts,
2000; Saliba et al., 2001). At isotopic equilibrium, N2O4 is enriched in 15N compared to NO and
NO2 (Walters & Michalski, 2015). Therefore, their measured α(NO2-NO) might be slightly higher
than the actual α(NO2-NO) value. In this work, the chamber wall was made of Teflon, which
showed minimum NO2 wall reactions and the low NOx mixing ratio minimized N2O4 formation.
Therefore, we suggest our measured α(NO2-NO) value (1.0275±0.0012) should better reflect the
NO-NO2 EIE in the atmosphere.

3.2. Kinetic isotopic fractionation of Leighton Cycle

The photochemical reactions of NOx complicate the isotopic fractionations between NO
and NO2. Since there were no VOCs or OH sources in the chamber (the photolysis of O3 as the
OH precursor is minor at the wavelength of blacklights used in the chamber), the formation of RO2
and HO2 can be neglected, and the NO-NO2 photochemistry cycle in the chamber was controlled
by NO2 photolysis and the NO + O3 reaction. Hence the KIE (R3-R4) and the PHIFE in R5-R6
were competing with the EIE between NO and NO2 (R1-R2):

14NO2→14NO+O             R3, rate constant=j(NO2)
15NO2→15NO+O             R4, rate constant=j(NO2)×α1
In which \( j(\text{NO}_2) \) is the \( \text{NO}_2 \) photolysis rate \((1.4 \times 10^{-3} \text{ s}^{-1} \text{ in the experiments})\), \( k_5 \) is the rate constant for the \( \text{NO} + \text{O}_3 \) reaction \((1.73 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}, \text{Atkinson et al., 2004})\), and \( \alpha_{1,2} \) are isotopic fractionation factors of the two reactions. Previous studies (Freyer et al., 1993; Walters et al., 2016) have attempted to assess the competition between EIE (R1-R2), KIE and PHIFE (R3-R6), but none of them quantified the relative importance of the two processes, nor were \( \alpha_1 \) or \( \alpha_2 \) values determined. Here we provide the mathematical solution of EIE, KIE and PHIFE to illustrate how R1-R6 affect the isotopic fractionations between \( \text{NO} \) and \( \text{NO}_2 \).

To demonstrate the competition between R1-R2 and R3-R6, we define:

\[
A = \begin{cases} 
\frac{\tau_{\text{exchange}}}{\tau_{\text{photo}}} & \text{when } j(\text{NO}_2) \neq 0 \\
0 & \text{when } j(\text{NO}_2) = 0 
\end{cases}
\]

Eq. (4)

in which \( \tau_{\text{exchange}} \) is the \( \text{NO}_2 \) lifetime with respect to isotopic exchange with \( \text{NO} \) and \( \tau_{\text{photo}} \) is the \( \text{NO}_2 \) lifetime with respect to photolysis:

\[
\tau_{\text{exchange}} = \frac{1}{k_5 \times [\text{NO}]} 
\]

Eq. (5)

\[
\tau_{\text{photo}} = \frac{1}{j(\text{NO}_2)} 
\]

Eq. (6)

The expression for \( A \), R1-R6 and Eq. (1)-(6) were used to derive the \( \delta(\text{NO}_2)-\delta(\text{NO}) \) and \( \delta(\text{NO}_2)-\delta(\text{NO}_x) \) values at steady state (see calculation in supplementary material):

\[
\delta(\text{NO}_2) - \delta(\text{NO}) \ (\%o) = \frac{(\alpha_2 - \alpha_1) \times A + (A(\text{NO}_2 - \text{NO}) - 1)}{A + 1} \times 1000 \ \%o 
\]

Eq. (7)

\[
\delta(\text{NO}_2) - \delta(\text{NO}_x) \ (\%o) = \frac{(\alpha_2 - \alpha_1) \times A + (A(\text{NO}_2 - \text{NO}) - 1)}{A + 1} \times (1 - f(\text{NO}_2)) \times 1000 \ \%o 
\]

Eq. (8)
Equation (7) shows the isotopic fractionation between NO and NO$_2$ ($\delta$(NO$_2$)-$\delta$(NO)) is determined by $A$, the EIE factor ($a$(NO$_2$-NO)-1) and the ($\alpha_2$-$\alpha_1$) factor. This ($\alpha_2$-$\alpha_1$) factor represents a combination of KIE and PHIFE, suggesting they act together as one factor; therefore, we name the ($\alpha_2$-$\alpha_1$) factor LCIE (Leighton Cycle Isotopic Effect). Using measured $\delta$(NO$_2$)-$\delta$(NO) values, $A$ values, and the previously determined EIE factor, we calculated that the best fit for the LCIE factor was -10±5‰ (Fig. 1B). The uncertainties in the LCIE factor were relatively higher than that of the EIE factor, mainly because of the accumulated analytical uncertainties at low NO$_x$ and O$_3$ concentrations, and low $A$ values (0.10-0.28) due to the relatively low $j$(NO$_2$) value ($1.4\times10^{-3}$ s$^{-1}$) under the chamber irradiation conditions.

We propose that our equations can be applied in the ambient environment to calculate the combined isotopic fractionations of EIE and LCIE between NO and NO$_2$. First, the NO$_2$ sinks (mainly NO$_2$+OH in the daytime) were at least 2-3 orders of magnitude slower than the Leighton Cycle and the NO-NO$_2$ isotopic exchange (Walters et al., 2016), therefore their effects on the $\delta$(NO$_2$) should be insignificant. Second, although the conversion of NO to NO$_2$ in the ambient environment is also controlled by NO + RO$_2$ and HO$_2$ in addition to NO+O$_3$, Eq. (7) still showed good agreement with field observations in previous studies, suggesting the NO+RO$_2$/HO$_2$ reactions might have similar fractionation factors as NO+O$_3$. Freyer et al. (1993) measured the annual average daytime $\delta$(NO$_2$)-$\delta$(NO) at Julich, Germany along with average daytime NO concentration (9 nmol mol$^{-1}$, similar to our experimental conditions) to be +18.03±0.98‰. Using Eq. (7), assuming the daytime average $j$(NO$_2$) value throughout the year was 5.0±1.0×10$^{-3}$, and a calculated $A$ value from measured NO$_x$ concentration ranged from 0.22-0.33, the average NO-NO$_2$ fractionation factor was calculated to be +18.8±1.4‰ (Fig. 1B), in excellent agreement with the measurements in the present study. Therefore, in the following discussion we will use this...
laboratory determined LCIE factor (-10 ‰) to calculate the nitrogen isotopic fractionation between NO and NO₂ at various atmospheric conditions.

3.3 Calculating nitrogen isotopic fractionations of NO-NO₂

We first used Eq. (7) to calculate the NO-NO₂ isotopic fractionations (δ(NO₂)-δ(NO)) at a wide range of NOₓ concentrations, f(NO₂) and j(NO₂) values (Fig. 2A-D). j(NO₂) values of 0 (Fig. 2A), 1.4×10⁻³ (Fig. 2B), 5×10⁻³ (Fig. 2C) and 1×10⁻² (Fig. 2D) were selected to represent nighttime, dawn (as well as the laboratory conditions of our experiments), daytime average and noon, respectively. Each panel represented a fixed j(NO₂) value, and the δ(NO₂)-δ(NO) were calculated as a function of the A value, which was derived from NOₓ concentration and f(NO₂). The A values have a large span, from 0 to 500, depending on the j(NO₂) value and the NO concentration. When A=0 (j(NO₂)=0) and f(NO₂)<1 (meaning NO-NO₂ coexist and [O₃]=0), Eq. (7) and (8) become Eq. (2) and (3), showing the EIE was the sole factor, the δ(NO₂)-δ(NO) values were solely controlled by EIE which has a constant value of +27.5 ‰ (Fig. 2A). When j(NO₂)>0, the calculated δ(NO₂)-δ(NO) values showed a wide range from -10.0 ‰ (controlled by LCIE factor: α₂-α₁=-10 ‰) to +27.5 ‰ (controlled by EIE factor: α(NO₂-NO)-1=+27.5 ‰). Fig. 2B-D display the transition from a LCIE-dominated regime to an EIE-dominated regime. The LCIE-dominated regime is characterized by low [NOₓ] (<50 pmol mol⁻¹), representing remote ocean areas and polar regions (Beine et al., 2002; Custard et al., 2015). At this range the A value can be greater than 200, thus Eq. (7) can be simplified as: δ(NO₂)-δ(NO)=(α₂-α₁)×1000 ‰, suggesting the LCIE almost exclusively controls the NO-NO₂ isotopic fractionation. The δ(NO₂)-δ(NO) values of these regions are predicted to be <0 ‰ during most time of the day and <5 ‰ at noon. On the other hand, the EIE-dominated regime was characterized by high [NOₓ] (>20 nmol mol⁻¹) and low f(NO₂) (<0.6), representative of regions with intensive NO emissions, e.g., roadside (Clapp & Jenkin, 2001;
Kimbrough et al., 2017). In this case, the $\tau_{\text{exchange}}$ are relatively short (10-50 s) compared to the $\tau_{\text{photo}}$ (approximately 100 s at noon and 1000 s at dawn), therefore the A values are small (0.01-0.5). The EIE factor in this regime thus is much more important than the LCIE factor, resulting in high $\delta(\text{NO}_2)$-$\delta(\text{NO})$ values (>20 ‰). Between the two regimes, both EIE and LCIE are competitive and therefore it is necessary to use Eq. (7) to quantify the $\delta(\text{NO}_2)$-$\delta(\text{NO})$ values.

Fig. 2 also implies that changes in the $j(\text{NO}_2)$ value may cause the diurnal variations in $\delta(\text{NO}_2)$-$\delta(\text{NO})$ and $\delta(\text{NO}_2)$-$\delta(\text{NO}_x)$ values. Changing $j(\text{NO}_2)$ would affect the value of A (Eq. (4)), consequently the NO-NO$_2$ isotopic fractionations in two ways: 1) changes in $j(\text{NO}_2)$ value would change the photolysis intensity, therefore the $\tau_{\text{photo}}$ value; 2) in addition, changes in $j(\text{NO}_2)$ value would also alter the steady state NO concentration, therefore changing the $\tau_{\text{exchange}}$ (Fig. 2C). The combined effect of these two factors on the A value varies along with the atmospheric conditions, and thus needs to be carefully calculated using NO$_x$ concentration data and/or atmospheric chemistry models.

We then calculated the differences of $\delta^{15}$N values between NO$_2$ and NO$_x$ emissions ($\delta(\text{NO}_2)$-$\delta(\text{NO}_x)$, Fig. 2E-H). Since $\delta(\text{NO}_2)$-$\delta(\text{NO}_x)$ are connected through the observed $\delta^{15}$N of NO$_2$ (or nitrate) to the $\delta^{15}$N of NO$_x$ emissions, this term might be useful in field studies (e.g., Chang et al., 2018; Zong et al., 2017). The calculated $\delta(\text{NO}_2)$-$\delta(\text{NO}_x)$ values (Fig. 2E-H) also showed a LCIE-dominated regime at low [NO$_x$] and an EIE-dominated regime at high [NO$_x$]. The $\delta(\text{NO}_2)$-$\delta(\text{NO}_x)$ values were dampened by the 1-$f(\text{NO}_2)$ factor comparing to $\delta(\text{NO}_2)$-$\delta(\text{NO})$, as shown in Eq. (3) and (8): $\delta(\text{NO}_2)$-$\delta(\text{NO}_x)$ = ($\delta(\text{NO}_2)$-$\delta(\text{NO})$)×(1-$f(\text{NO}_2)$). At high $f(\text{NO}_2)$ values (>0.8), the differences between $\delta(\text{NO}_2)$ and $\delta(\text{NO}_x)$ were less than 5 ‰, thus the measured $\delta(\text{NO}_2)$ values were similar to $\delta(\text{NO}_x)$, although the isotopic fractionation between NO and NO$_2$ could be noteworthy. Some ambient environments with significant NO emissions or high NO$_2$ photolysis
rates usually have \( f(\text{NO}_2) \) values between 0.4-0.8 (Mazzeo et al., 2005; Vicars et al., 2013). In this scenario, the \( \delta(\text{NO}_2)-\delta(\text{NO}_x) \) values in Fig. 2F-H showed wide ranges of -4.8 ‰ to +15.6 ‰, -6.0 ‰ to +15.0 ‰, and -6.3 ‰ to +14.2 ‰ at \( j(\text{NO}_2)=1.4\times10^{-3} \text{ s}^{-1}, 5\times10^{-3} \text{ s}^{-1}, 1\times10^{-2} \text{ s}^{-1} \), respectively. These significant differences again highlighted the importance of both LCIE and EIE (Eq. (7) and (8)) in calculating the \( \delta(\text{NO}_2)-\delta(\text{NO}_x) \).

4. Implications

We first assessed the daily variation of \( \delta(\text{NO}_2)-\delta(\text{NO}_x) \) values at two roadside \( \text{NO}_x \) monitoring sites. Hourly NO and \( \text{NO}_2 \) concentrations was acquired from two sites at Anaheim, CA (https://www.arb.ca.gov) and Evansville, IN (http://idem.tx.sutron.com) on July 25, 2018, then we used \( j(\text{NO}_2) \) values output from TUV model (Madronich & Flocke, 1999) at these locations to calculate the daily variations of \( \delta(\text{NO}_2)-\delta(\text{NO}_x) \) values (Fig. 3A, B) using Eq. (8). Hourly \( \text{NO}_x \) concentrations were 12-51 nmol mol\(^{-1}\) at Anaheim and 9-38 nmol mol\(^{-1}\) at Evansville and the \( f(\text{NO}_2) \) values at both sites did not show significant daily variations (0.45±0.07 at Anaheim and 0.65±0.08 at Evansville), likely because the \( \text{NO}_x \) concentrations were controlled by the high NO emissions from the road (Gao, 2007). Assuming steady state isotopic fractionation was reached, the calculated \( \delta(\text{NO}_2)-\delta(\text{NO}_x) \) values showed significant diurnal variations. During the nighttime, the isotopic fractionations were solely controlled by the EIE, the \( \delta(\text{NO}_2)-\delta(\text{NO}_x) \) values were +14.5±2.0 ‰ and +8.7±2.1 ‰ at Anaheim and Evansville, respectively. During the daytime, the existence of LCIE lowered the \( \delta(\text{NO}_2)-\delta(\text{NO}_x) \) values to +9.8±1.7 ‰ at Anaheim and +3.1±1.5 ‰ at Evansville while the \( f(\text{NO}_2) \) values at both sites remained similar. The lowest \( \delta(\text{NO}_2)-\delta(\text{NO}_x) \) values for both sites (+7.0 ‰ and +1.7 ‰) occurred around noon when the \( \text{NO}_x \) photolysis was the most intense. In contrast, if one neglects the LCIE factor in the daytime, the \( \delta(\text{NO}_2)-\delta(\text{NO}_x) \)
values would be $+12.9\pm 1.5 \, \%$ and $+10.0\pm 1.6 \, \%$ respectively, an overestimation of 3.1 \, \% and 6.9 \, \%. These discrepancies suggested that the LCIE played an important role in the NO-NO$_2$ isotopic fractionations and neglecting it could bias the NO$_x$ source apportionment using $\delta^{15}$N of NO$_2$ or nitrate.

The role of LCIE was more important in less polluted sites. We calculated the $\delta$(NO$_2$)-$\delta$(NO$_x$) values (assuming steady state isotopic fractionation) at suburban San Diego, CA, USA, again using the hourly NO$_x$ concentrations (https://www.arb.ca.gov, Fig. 3C) and $j$(NO$_2$) values calculated from the TUV model. NO$_x$ concentrations at this site varied from 1 to 9 nmol mol$^{-1}$.

During the nighttime, NO$_x$ was in the form of NO$_2$ ($f$(NO$_2$) = 1) because O$_3$ concentrations were higher than NO$_x$, thus the $\delta$(NO$_2$) values should be identical to $\delta$(NO$_x$). In the daytime a certain amount of NO was produced by direct NO emission and NO$_2$ photolysis but the $f$(NO$_2$) was still high (0.73$\pm$0.08). Our calculation suggested the daytime $\delta$(NO$_2$)-$\delta$(NO$_x$) values should be only $+1.3\pm 3.2 \, \%$ with a lowest value of -1.3 \, \%. These $\delta$(NO$_2$)-$\delta$(NO$_x$) values agree well with the observed and modelled summer daytime $\delta$(NO$_2$) values in West Lafayette, IN (Walters et al., 2018), which suggest the average daytime $\delta$(NO$_2$)-$\delta$(NO$_x$) values at NO$_x$ = 3.9$\pm$1.2 nmol mol$^{-1}$ should range from +0.1 \, \% to +2.4 \, \%. In this regime, we suggest the $\delta$(NO$_2$)-$\delta$(NO$_x$) values were generally small due to the significant contribution of LCIE and high $f$(NO$_2$).

The LCIE should be the dominant factor controlling the NO-NO$_2$ isotopic fractionation at remote regions, resulting in a completely different diurnal pattern of $\delta$(NO$_2$)-$\delta$(NO$_x$) compared with the urban-suburban area. Direct hourly measurements of NO$_x$ at remote sites are rare, thus we used total NO$_x$ concentration of 50 pmol mol$^{-1}$, daily O$_3$ concentration of 20 nmol mol$^{-1}$ at Summit, Greenland (Dibb et al., 2002; Hastings et al., 2004; Honrath et al., 1999; Yang et al., 2002), and assumed the conversion of NO to NO$_2$ was completely controlled by O$_3$ to calculate
the NO/NO\textsubscript{2} ratios. Here the isotopes of NO\textsubscript{x} were almost exclusively controlled by the LCIE due to the high A values (>110). The \(\delta(\text{NO}_2) - \delta(\text{NO}_3)\) values displayed a clear diurnal pattern (Fig. 3D) with highest value of -0.3 \% in the “nighttime” (solar zenith angle >85 degree) and lowest value of -5.0 \% in the mid-day. This calculated daily variation of 4.7 \% was similar to the observed \(\delta^{15}\text{N}\) of nitrate (\(\delta(\text{NO}_3)\)) in near-surface snow: Hastings et al. (2004) found that \(\delta(\text{NO}_3)\) of samples collected at early night (19:30) was 4-5 \% lower than those collected at early morning (07:00).

Since the nitrate samples were collected from the near surface, we suggest that the early night samples should represent nitrate accumulated in the daytime, and the morning samples should represent the nitrate formed in the “nighttime”. This observation was in general agreement with our prediction, indicating that the \(\delta(\text{NO}_2)\) might played an important role in determining the \(\delta(\text{NO}_3)\). However, since the isotopic fractionation factors of nitrate-formation reactions (\(\text{NO}_2 + \text{OH}\), \(\text{NO}_3 + \text{HC}\), \(\text{N}_2\text{O}_5 + \text{H}_2\text{O}\)) are still unknown, more studies are needed to fully explain the daily and seasonal variations of \(\delta(\text{NO}_3)\) at remote regions.

5. Conclusions

We investigated the effect of NO\textsubscript{x} photochemistry on the nitrogen isotopic fractionations between NO and NO\textsubscript{2}. We first mathematically calculated the combined effects of EIE (equilibrium isotopic fractionation caused by NO-NO\textsubscript{2} isotopic exchange) and LCIE (Leighton Cycle induced isotopic fractionations) to demonstrate that the relative importance of EIE and LCIE depends on NO, NO\textsubscript{2} concentrations and \(j(\text{NO}_2)\) value (Eq. (7) and Eq. (8)). We then measured the isotopic fractionation factors of EIE and LCIE at room temperature to be 1.0275\pm0.0012 and 0.990\pm0.005, respectively. These calculations and measurements enabled us to calculate the steady state \(\delta(\text{NO}_2) - \delta(\text{NO})\) and \(\delta(\text{NO}_2) - \delta(\text{NO}_3)\) values at any given condition. Subsequently we applied
our equations to polluted, clean and remote sites to model the daily variations of $\delta$(NO$_2$)-$\delta$(NO$_x$) values. We found that the $\delta$(NO$_2$)-$\delta$(NO$_x$) values could vary from over +20 ‰ to less than -5 ‰ depending on the environment: in general, the role of LCIE becoming more important at low NO$_x$ concentrations, which tend to decrease the $\delta$(NO$_2$)-$\delta$(NO$_x$) values. Our work provided a mathematical approach to quantify the nitrogen isotopic fractionations between NO and NO$_2$ that can be applied to many conditions, which could help interpret the measured $\delta^{15}$N values of NO$_2$ and nitrate in field observation studies.

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Data Availability

Data acquired from this study was deposited at Open Sciences Framework (Li, 2019, DOI 10.17605/OSF.IO/JW8HU).

Author contribution

J. Li and G. Michalski designed the experiments, X. Zhang and J. Li conducted the experiments. X. Zhang, G. Michalski, J. Orlando and G. Tyndall helped J. Li in interpreting the results. The manuscript was written by J. Li and all the authors have contributed during the revision of this manuscript.

Competing interest

The authors declare no competing interest.
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Fig. 1 δ¹⁵N of NO₂ collected in dark and UV irradiation experiments. A. Results from five dark experiments yielded a line with $\varepsilon$(NO₂-NO)/(1+$\varepsilon$(NO₂-NO)) value of 26.8 ‰ and $\varepsilon$(NO₂-NO) value of 27.5 ‰; B. Results from five UV irradiation experiments (black points) and a previous field study (red triangle). The three lines represent different (α₂-α₁) values: the (α₂-α₁)=-10 ‰ line showed the best fit to our experimental data as well as the previous field observation.
Fig. 2 Calculating isotopic fractionation values between NO-NO$_2$ ($\delta$(NO$_2$) - $\delta$(NO), A-D) and NO$_x$-NO$_2$ ($\delta$(NO$_2$) - $\delta$(NO$_x$), E-H) at various j(NO$_2$), NO$_x$ level and j(NO$_2$) using Eq. (7) and (8). Each panel represents a fixed j value (showing on the upper right side of each panel), and the fractionation values are shown by color. Lines are contours with constant fractionation values and each number on the contour represents its value.
Fig. 3 NOx concentrations and calculated δ(NO2)-δ(NOx) values at four sites. Stacked bars show the NO and NO2 concentrations extracted from monitoring sites (A-C) or calculated using 0-D box model (D); the red lines are δ(NO2)-δ(NOx) values at each site.