Quantifying the nitrogen isotope effects during photochemical equilibrium between NO and NO$_2$: implications for $\delta^{15}$N in tropospheric reactive nitrogen

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Abstract. Nitrogen isotope fractionations between nitrogen oxides (NO and NO$_2$) play a significant role in determining the nitrogen isotopic compositions ($\delta^{15}$N) of atmospheric reactive nitrogen. Both the equilibrium isotopic exchange between NO and NO$_2$ molecules and the isotope effects occurring during the NO$_x$ photochemical cycle are important, but both are not well constrained. The nighttime and daytime isotopic fractionations between NO and NO$_2$ in an atmospheric simulation chamber at atmospherically relevant NO$_x$ levels were measured. Then, the impact of NO$_x$ level and NO$_2$ photolysis rate on the combined isotopic fractionation (equilibrium isotopic exchange and photochemical cycle) between NO and NO$_2$ was calculated. It was found that the isotope effects occurring during the NO$_x$ photochemical cycle can be described using a single fractionation factor, designated the Leighton cycle isotope effect (LCIE). The results showed that at room temperature, the fractionation factor of nitrogen isotopic exchange is 1.0289 ± 0.0019, and the fractionation factor of LCIE (when O$_3$ solely controls the oxidation from NO to NO$_2$) is 0.990 ± 0.005. The measured LCIE factor showed good agreement with previous field measurements, suggesting that it could be applied in an ambient environment, although future work is needed to assess the isotopic fractionation factors of NO + RO$_2$/HO$_2$ → NO$_2$. The results were used to model the NO–NO$_2$ isotopic fractionations under several NO$_x$ conditions. The model suggested that isotopic exchange was the dominant factor when NO$_x$ > 20 nmol mol$^{-1}$, while LCIE was more important at low NO$_x$ concentrations (< 1 nmol mol$^{-1}$) and high rates of NO$_2$ photolysis. These findings provided a useful tool to quantify the isotopic fractionations between tropospheric NO and NO$_2$, which can be applied in future field observations and atmospheric chemistry models.

1 Introduction

The nitrogen isotopic composition (δ$^{15}$N) of reactive nitrogen compounds in the atmosphere is an important tool in understanding the sources and chemistry of atmospheric NO$_x$ (NO + NO$_2$). It has been suggested that the δ$^{15}$N value of atmospheric nitrate (HNO$_3$, nitrate aerosols and nitrate ions in precipitation and snow) imprints the δ$^{15}$N value of NO$_x$ sources (Elliott et al., 2009; Kendall et al., 2007); thus many studies have used the δ$^{15}$N values of atmospheric nitrate to investigate NO$_x$ sources (Chang et al., 2018; Felix et al., 2012; Felix and 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 that may occur during photochemical cycling of NO$_x$ could alter the δ$^{15}$N values as it partitions into NO$_y$ (NO$_3$ = atmospheric nitrate, NO$_3$, N$_2$O$_5$, HONO, etc.; 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). Similarly, other complex reactive nitrogen chemistry, such as nitrate photolysis and rede-
position in ice and snow (Frey et al., 2009), may impact the δ15N of NOx and atmospheric nitrate. The fractionation between NO and NO2 via isotope exchange has been suggested to be the dominant factor in determining the δ15N of NO2 and ultimately atmospheric nitrate (Freyer, 1991; Freyer et al., 1993; Savarino et al., 2013; Walters et al., 2016). However, isotopic fractionations occur in most, if not all, NOx and NOy reactions, while most of these are still unknown or, if calculated (Walters and Michalski, 2015), unverified by experiments. Since the atmospheric chemistry of NOx varies significantly in different environments (e.g., polluted vs. pristine, night vs. day), the isotopic fractionations associated with NOy chemistry are also likely to vary in different environments. These unknowns could potentially bias conclusions about NOx source apportionment reached when using nitrogen isotopes. Therefore, understanding the isotopic fractionations between NO and NO2 during photochemical cycling could improve our understanding of the relative role of sources versus chemistry for controlling the δ15N variations in atmospheric NO2 and nitrate.

In general, there are three types of isotopic fractionation effects associated with NOx chemistry (Fig. 1a). The first type is the equilibrium isotopic effect (EIE), i.e., isotope exchange between two compounds without forming new molecules (Urey, 1947; Bigeleisen and Mayer, 1947), which for nitrogen isotopes in the NOx system is the 15NO+14NO2 ↔ 14NO+15NO2 exchange reaction (Begun and Melton, 1956; Walters et al., 2016). The second type is the kinetic isotopic effect (KIE) associated with difference in isotopologue rate coefficients during unidirectional reactions (Bigeleisen and Wolfsberg, 1957). In the NOx system this KIE would manifest in the oxidation of NO into NO2 by O3/HO2/RO2. The third type is the photochemical isotope fractionation effect (PHIFE; Miller and Yung, 2000), which for NOx is the isotopic fractionation associated with NOx photolysis. All three fractionations could impact the δ15N value of NO2 and consequently atmospheric nitrate, but the relative importance of each may vary.

The limited number of studies on the EIE in the NOx cycle have significant uncertainties. Discrepancies in the EIE for 15NO+14NO2 ↔ 14NO+15NO2 have been noted in several studies. Theoretical calculations predicted isotope fractionation factors (α) ranging from 1.035 to 1.042 at room temperature (Begun and Fletcher, 1960; Monse et al., 1969; Walters and Michalski, 2015) due to the different approximations used to calculate harmonic frequencies in each study. Likewise, two separate experiments measured different room temperature fractionation factors of 1.028 ± 0.002 (Begun and Melton, 1956) and 1.0356 ± 0.0015 (Walters et al., 2016). A concern in both experiments is that they were conducted in small chambers with high NOx concentrations (hundreds of micromoles per mole), significantly higher than typical ambient atmospheric NOx levels (usually less than 0.1 µmol mol⁻¹). Whether the isotopic fractionation factors determined by these experiments are applicable in the ambient environment is uncertain because of possible wall effects and formation of higher oxides, notably N2O4 and N2O3 at these high NOx concentrations.

Even less research has examined the KIE and PHIFE occurring during NOx cycling. The KIE of NO + O3 has been theoretically calculated (Walters and Michalski, 2016) but has not been experimentally verified. The NO2 PHIFE has not been experimentally determined or theoretically calcu-
lated. As a result, field observation studies often overlook the effects of PHIFE and KIE. Freyer et al. (1993) measured NO\textsubscript{x} concentrations and the δ\textsuperscript{15}N values of NO\textsubscript{2} over a 1-year period at Julich, Germany, and inferred a combined NO\textsubscript{x} isotope fractionation factor \((EIE+KIE+PHIFE)\) of 1.018 ± 0.001. Freyer et al. (1993) suggested that the NO\textsubscript{2} photochemical cycle \((KIE\text{ and } PHIFE)\) tends to diminish the equilibrium isotopic fractionation \((EIE)\) between NO and NO\textsubscript{2}. Even if this approach was valid, applying this single fractionation factor elsewhere, where NO\textsubscript{x} and O\textsubscript{3} concentrations and actinic fluxes are 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 various tropospheric conditions, it is crucial to know (1) isotopic fractionation factors of EIE, KIE and PHIFE individually and (2) the relative importance of each factor under various conditions.

In this work, we aim to quantify the nitrogen isotope fractionation factors between NO and NO\textsubscript{2} at photochemical equilibrium. First, we measure the N isotope fractionations at several sites to illustrate the behavior of δ\textsuperscript{15}N values of NO\textsubscript{x} in the ambient environment.

2 Methods

The experiments were conducted using a 10 m\textsuperscript{3} atmospheric simulation chamber at the National Center for Atmospheric Research (see descriptions in Appendix A and Zhang et al., 2018). A set of mass flow controllers was used to inject NO and O\textsubscript{3} into the chamber. NO was injected at 1 L min\textsuperscript{-1} from an in-house NO/N\textsubscript{2} cylinder (133.16 µmol mol\textsuperscript{-1} NO in ultrapure N\textsubscript{2}), and O\textsubscript{3} was generated by flowing zero air through a flow tube equipped with a UV Pen-Ray lamp (UVP LLC., CA) into the chamber at 5 L min\textsuperscript{-1}. NO and NO\textsubscript{2} concentrations were measured in real time by chemiluminescence with a detection limit of 0.5 nmol mol\textsuperscript{-1} (model CLD 88Y, Eco Physics, MI) as were O\textsubscript{3} concentrations using a UV absorption spectroscopy with a detection limit of 0.5 nmol mol\textsuperscript{-1} (model 49, Thermo Scientific, CO). In each experiment, the actual amounts of NO and O\textsubscript{3} injected were calculated using measured NO\textsubscript{x} and O\textsubscript{3} concentrations after a steady state was reached (usually within 1 h). The wall loss rate of NO\textsubscript{2} was tested by monitoring O\textsubscript{3} \((29 \text{ nmol mol}^{-1})\) and NO\textsubscript{x} \((62 \text{ nmol mol}^{-1})\) over a 4 h period. After the NO and NO\textsubscript{2} concentrations reached a steady state, no decrease in NO\textsubscript{2} concentrations was observed, showing that chamber wall loss was negligible.

Three experiments were conducted to measure the δ\textsuperscript{15}N value of the tank NO (i.e., the δ\textsuperscript{15}N value of total NO\textsubscript{x}). In each of these experiments, a certain amount of O\textsubscript{3} was first injected into the chamber, then approximately the same amount of NO was injected into the chamber to ensure 100% of the NO\textsubscript{x} was in the form of NO\textsubscript{2} with little O\textsubscript{3} (< 15 nmol mol\textsuperscript{-1}) remaining in the chamber such that the O\textsubscript{3} + NO\textsubscript{2} reaction was negligible. The NO\textsubscript{2} in the chamber was then collected and its δ\textsuperscript{15}N value measured, which equates to the δ\textsuperscript{15}N value of the tank NO.

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 of these dark experiments, a range of NO and O\textsubscript{3} \(([O_3] < [NO])\) was injected into the chamber to produce NO–NO\textsubscript{2} mixtures with [NO]/[NO\textsubscript{2}] ratios ranging from 0.43 to 1.17. The N isotopes of these mixtures were used to investigate the EIE between NO and NO\textsubscript{2}. The second set of experiments was conducted under irradiation of UV lights (300–500 nm; see Appendix A for irradiation spectrum). Under such conditions, NO, NO\textsubscript{2} and O\textsubscript{3} reached a photochemically steady state, which combined the isotopic effects of EIE, KIE and PHIFE.

In all experiments, the concentrations of NO, NO\textsubscript{2} and O\textsubscript{3} were allowed to reach a steady state, and the product NO\textsubscript{2} was collected from the chamber using a honeycomb denuder tube. After the NO, NO\textsubscript{2} and O\textsubscript{3} concentrations reached a steady state, well-mixed chamber air was drawn out through a 40 cm long Norprene thermoplastic tubing at 10 L min\textsuperscript{-1} and passed through a honeycomb denuder system (Chemicomb 3500, Thermo Scientific). Based on flow rate, the NO\textsubscript{2} residence time in the tubing was less than 0.5 s; thus in the light-on experiments where NO and O\textsubscript{3} coexisted, the NO\textsubscript{2} produced inside the transfer tube through NO + O\textsubscript{3} reactions should be < 0.03 nmol mol\textsuperscript{-1} (using the upper limit of NO and O\textsubscript{3} concentrations in our experiments). The honeycomb denuder system consisted of two honeycomb denuder tubes connected in series. Each honeycomb denuder tube is a glass cylinder 38 mm long and 47 mm in diameter and consists of 212 hexagonal tubes with inner diameters of 2 mm. Before collecting samples, each denuder tube was coated with a solution of 10 % KOH and 25 % guaiacol in methanol and then dried by flowing N\textsubscript{2} gas through the denuder tube for 15 s (Williams and Grosjean, 1990; Walters et al., 2016). The NO\textsubscript{2} reacted with the guaiacol coating and was converted into NO\textsubscript{2} that was retained on the denuder tube wall (Williams and Grosjean, 1990). NO\textsubscript{2} was inert to the denuder tube coating: a control experiment sampled pure NO using the denuder tubes, which did not show any measurable NO\textsubscript{2}. The NO\textsubscript{2} collection efficiency of a single honeycomb denuder tube was tested in another control experiment: air containing 66 nmol mol\textsuperscript{-1} of NO\textsubscript{2} was drawn out of the chamber through a denuder tube, and the NO\textsubscript{2} concentration at the exit of the tube holder was measured...
and found to be below the detection limit (< 1 nmol mol\(^{-1}\)), suggesting that the collection efficiency was nearly 100% when [NO\(_2\)] < 66 nmol mol\(^{-1}\). Furthermore, when the denuder system consisted of two denuder tubes in series, NO\(_2\) in the second denuder was below the detection limit, indicating trivial NO\(_2\) breakthrough. Each NO\(_2\) collection lasted for 0.5–3 h in order to collect enough NO\(_2\) for isotopic analysis (at least 300 nmol). After collection, the NO\(_2\) was leached from each denuder tube by rinsing thoroughly with 10 mL deionized water into a clean polypropylene container and stored frozen until isotopic analysis. Isotopic analysis was conducted at the Purdue Stable Isotope Laboratory. For each sample, approximately 50 nmol of the NO\(_2\) extract was mixed with 2 M sodium azide solution in an acetic acid buffer in airtight glass vial, then shaken overnight to completely reduce all the NO\(_2\) to N\(_2\)O\(_5\) (Casciotti and McIlvin, 2007; McIlvin and Altabet, 2005). The product N\(_2\)O was directed into a Thermo Scientific GasBench equipped with a cryotrap, then the \(\delta^{15}N\) of the N\(_2\)O was measured using a Delta-V isotope ratio mass spectrometer (IRMS). Six coated denuder tubes that did not get exposed to NO\(_2\) were also analyzed using the same chemical procedure, which did not show any measurable signal on the IRMS, suggesting that the blank from both the sampling process and the chemical conversion process was negligible. The overall analytical uncertainty for \(\delta^{15}N\) analysis was 0.5\% \((1\sigma)\) based on replicate analysis of in-house NO\(_2\) standards.

3 Results and discussions

3.1 Equilibrium isotopic fractionation between NO and NO\(_2\)

The equilibrium isotope fractionation factor, \(\alpha\) (NO\(_2\)–NO), is the \(\delta^{15}N\) enrichment in NO\(_2\) relative to NO and is expressed as the ratio of rate constants \(k_2/k_1\) of two reactions:

\[
\begin{align*}
\text{NO}_2 + ^{14}\text{NO} \rightarrow \text{NO} + ^{14}\text{NO}_2, \\
\text{rate constant} = k_1 \\
\text{NO} + ^{14}\text{NO}_2 \rightarrow \text{NO}_2 + ^{14}\text{NO}, \\
\text{rate constant} = k_2 = k_1 \alpha\text{NO}_2\text{–NO},
\end{align*}
\]

where \(k_1\) is the rate constant of the isotopic exchange, which was previously determined to be \(8.14 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}\) (Sharma et al., 1970). The reaction time required for NO–NO\(_2\) to reach isotopic equilibrium was estimated using the exchange rate constants in a simple kinetics box model (BOXMOX; Knote et al., 2015). The model predicts that at typical NO\(_x\) concentrations used during the chamber experiments (7.7–62.4 nmol mol\(^{-1}\)), isotopic equilibrium would be reached within 15 min (see Appendix B). Since the sample collection usually started 1 h after NO\(_x\) was well mixed in the chamber, there was sufficient time to reach full isotope equilibrium. The isotope equilibrium fractionation factor (\(\alpha\) (NO\(_2\)–NO)) is then calculated to be

\[
\alpha\text{NO}_2\text{–NO} = \frac{[^{15}\text{NO}_2][^{14}\text{NO}]}{[^{14}\text{NO}_2][^{15}\text{NO}]} = \frac{R\text{NO}_2}{R\text{NO}},
\]

where \(R\text{NO}_2\) are the \(^{15}\text{N}/^{14}\text{N}\) ratios of NO and NO\(_2\). By definition, the \(\delta^{15}N\text{NO} (\%) = (R\text{NO}/R\text{reference} - 1) \times 1000\%\), where \(\delta^{15}N\text{NO}_2\) is \((R\text{NO}_2)/R\text{reference} - 1) \times 1000\%\), but hereafter, the \(\delta^{15}N\) values of NO, NO\(_2\) and NO\(_x\) are referred to as \(\delta\text{NO}\), \(\delta\text{NO}_2\) and \(\delta\text{NO}_x\), respectively. Equation (1) leads to

\[
\delta\text{NO}_2 - \delta\text{NO} = (\alpha\text{NO}_2\text{–NO} - 1)(1 + \delta\text{NO}).
\]

Using Eq. (2) and applying NO\(_x\) isotopic mass balance (\(\delta\text{NO}_x = f\text{NO}_2\delta\text{NO}_2 + (1 - f\text{NO}_2)\delta\text{NO}\), \(f\text{NO}_2 = [\text{NO}_2]/([\text{NO}] + [\text{NO}_2])\)) yields

\[
\frac{\delta\text{NO}_2 - \delta\text{NO}_x}{1 + \text{NO}_2} = \frac{\alpha\text{NO}_2\text{–NO} - 1}{\alpha\text{NO}_2\text{–NO}}(1 - f\text{NO}_2).
\]

Here, \(\delta\text{NO}_x\) equals the \(\delta^{15}N\) value of the cylinder NO, and \(f\text{NO}_2\) is the molar fraction of NO\(_2\) with respect to total NO\(_x\). Three experiments (Table 1) that measured \(\delta\text{NO}_x\) showed consistent \(\delta\text{NO}_x\) values of \(-58.7 \pm 0.8\%\) (\(n = 3\)), indicating that \(\delta\text{NO}_x\) remained unchanged throughout the experiments (as expected for isotope mass balance). Thus, \(\delta\text{NO}_x\) can be treated as a constant in Eq. (3), and the linear regression of \((\delta\text{NO}_2 - \delta\text{NO}_x)/(1 + \delta\text{NO}_2)\) versus \(1 - f\text{NO}_2\) should have an intercept of 0 and a slope of \((\alpha\text{NO}_2\text{–NO} - 1)/\alpha\text{NO}_2\text{–NO}\).

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 an \(\alpha\text{NO}_2\text{–NO}\) value of 1.0289 ± 0.0019 at room temperature (Fig. 1b and Table 1). This fractionation factor is comparable to previously measured values but 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 \(\alpha\text{NO}_2\text{–NO}\) values of NO–NO\(_2\) exchange in a 1 L reaction vessel, which showed a slightly higher \(\alpha\text{NO}_2\text{–NO}\) value of 1.035. This discrepancy might originate from rapid heterogeneous reactions on the wall of the reaction vessel at high NO\(_x\) concentrations and the small chamber size used by Walters et al. (2016). They used a reaction vessel made of Pyrex, which is known to absorb water (Do Remus et al., 1983; Takei et al., 1997) and can react with NO\(_2\) forming HONO, HNO\(_3\) and other N compounds. Additionally, previous studies have suggested that Pyrex walls enhance the formation rate of N\(_2\)O by over an order of magnitude (Barney and Finlayson-Pitts, 2000; Saliba et al., 2001), which at isotopic equilibrium is enriched in \(^{15}N\) compared to NO and NO\(_2\) (Walters and Michalski, 2015). Therefore, their measured \(\alpha\text{NO}_2\text{–NO}\) might be slightly higher than the actual \(\alpha\text{NO}_2\text{–NO}\) value. In this work, the 10 m\(^3\) chamber has a much smaller surface-volume ratio relative to Walters.
et al. (2016), which minimizes wall effects, and the walls were made of Teflon, which minimizes NO2 surface reactivity, as evidenced by the NO2 wall loss control experiment. Furthermore, the low NOx mixing ratios in our experiments minimized N2O4 and N2O5 formation. At NO and NO2 concentrations of 50 pmol mol\(^{-1}\), the steady-state concentrations of N2O4 and N2O5 were calculated to be 0.014 and 0.001 pmol mol\(^{-1}\), respectively (Atkinson et al., 2004). Therefore, we suggest that our measured \(\alpha\) (NO2–NO) value (1.0289 ± 0.0019) may better reflect the room temperature (298 K) NO–NO2 EIE in the ambient environment.

Unfortunately, the chamber temperature could not be controlled, so we were not able to investigate the temperature dependence of the EIE. Hence, we speculate that the \(\alpha\) (NO2–NO) follows a similar temperature dependence pattern calculated in Walters et al. (2016). Walters et al. (2016) suggested that the \(\alpha\) (NO2–NO) value would be 0.0047 higher at 273 K and 0.002 lower at 310 K relative to room temperature (298 K). Using this pattern and our experimentally determined data, we suggest that the \(\alpha\) (NO2–NO) values at 273, 298 and 310 K are 1.0336 ± 0.0019, 1.0289 ± 0.0019 and 1.0269 ± 0.0019, respectively. This 0.0067 variation at least partially contributes to the daily and seasonal variations in \(\delta^{15}\)N values of NO2 and nitrate in some areas (e.g., polar regions with strong seasonal temperature variation). Thus, future investigations should be conducted to verify the EIE temperature dependence.

### 3.2 Kinetic isotopic fractionation of Leighton cycle

The photochemical reactions of NOx will compete with the isotope exchange fractionations between NO and NO2. The NO–NO2 photochemical cycle in the chamber was controlled by the Leighton cycle: NO2 photolysis and the NO + O3 reaction. This is because there were no volatile organic compounds (VOCs) in the chamber, so no RO2 was produced, which excludes the NO + RO2 reaction. Likewise, the low water vapor content (relative humidity < 10%) and the minor flux of photons (< 310 nm) results in minimal OH production and hence little NO2 formation, and subsequently a trivial amount of NO2 would be formed by NO + HO2. Applying these limiting assumptions, the EIE between NO and NO2 (Reactions R1–R2) is only competing with the KIE (Reactions R3–R4) and the PHIFE in Reactions (R5)–(R6):

\[
\begin{align*}
14\text{NO}_2 & \rightarrow 14\text{NO} + \text{O}, \\
\text{rate constant} & = j (\text{NO}_2) \quad (R3) \\
15\text{NO}_2 & \rightarrow 15\text{NO} + \text{O}, \\
\text{rate constant} & = j (\text{NO}_2) \alpha_1 \quad (R4) \\
\text{NO} + \text{O}_3 & \rightarrow 14\text{NO}_2 + \text{O}_2, \\
\text{rate constant} & = k_5 \quad (R5) \\
15\text{NO} + \text{O}_3 & \rightarrow 15\text{NO}_2 + \text{O}_2, \\
\text{rate constant} & = k_5 \alpha_2. \quad (R6)
\end{align*}
\]

in which \(j (\text{NO}_2)\) is the NO2 photolysis rate \((1.4 \times 10^{-3} \text{ s}^{-1})\) in these experiments, \(k_5\) is the rate constant for the NO + O3 reaction \((1.73 \times 10^{-14} \text{ cm}^3 \text{s}^{-1});\) Atkinson et al., 2004), and \(\alpha_{1,2}\) are isotopic fractionation factors for the two reactions. Previous studies (Freyer et al., 1993; Walters et al., 2016) have attempted to assess the competition between EIE (Reactions R1–R2), KIE and PHIFE (Reactions R3–R6), but none of them quantified the relative importance of the two processes, nor were \(\alpha_1\) or \(\alpha_2\) values experimentally determined. Here we provide the mathematical solution of EIE, KIE and PHIFE to illustrate how Reactions (R1)–(R6) affect the isotopic fractionations between NO and NO2.
First, the NO2 lifetime with respect to isotopic exchange with NO ($\tau_{\text{exchange}}$) and photolysis ($\tau_{\text{photo}}$) was determined:

\[
\tau_{\text{exchange}} = \frac{1}{k_1[\text{NO}]},
\]

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

We then define an A factor:

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

Using Reactions (R1)–(R6) and Eqs. (1)–(6), we solved steady-state $\delta(\text{NO}_2)$ and $\delta(\text{NO})$ values (see calculations in Appendix C). Our calculations show that the $\delta(\text{NO}_2) - \delta(\text{NO})$ and $\delta(\text{NO}_2) - \delta(\text{NO}_2) = 0$ values at a steady state can be expressed as functions of $\alpha_1$, $\alpha_2$, $\alpha(\text{NO}_2-\text{NO})$ and $A$:

\[
\delta(\text{NO}_2) - \delta(\text{NO}) = \frac{(\alpha_2 - \alpha_1)A + (\alpha (\text{NO}_2-\text{NO}) - 1)}{(1 + \delta (\text{NO}_2))} \approx \frac{(\alpha_2 - \alpha_1)A + (\alpha (\text{NO}_2-\text{NO}) - 1)}{(1 + \delta (\text{NO}_2))}
\]

\[
\delta(\text{NO}_2) - \delta(\text{NO}_2) = \frac{(\alpha_2 - \alpha_1)A + (\alpha (\text{NO}_2-\text{NO}) - 1)}{(1 + \delta (\text{NO}_2))(1 - f(\text{NO}_2))} \approx \frac{(\alpha_2 - \alpha_1)A + (\alpha (\text{NO}_2-\text{NO}) - 1)}{(1 + \delta (\text{NO}_2))(1 - f(\text{NO}_2))}.
\]

Equation (7) shows the isotopic fractionation between NO and NO2: $\delta(\text{NO}_2) - \delta(\text{NO})$ is mainly determined by $A$; the EIE factor $\alpha(\text{NO}_2-\text{NO})$ and $\alpha_2 - \alpha_1$ factor assuming $1 + \delta (\text{NO}_2)$ is close to 1. This $\alpha_2 - \alpha_1$ represents a combination of KIE and PHIFE, suggesting that they act together as one factor; therefore, we name the $\alpha_2 - \alpha_1$ factor the Leighton cycle isotopic effect (LCIE). Using measured $\delta(\text{NO}_2)$ and $\delta(\text{NO}_2)$ values, $A$ values (Table 1), and the previously determined $\alpha(\text{NO}_2-\text{NO})$ value, we plot $\delta(\text{NO}_2) - \delta(\text{NO}) = \frac{(\alpha_2 - \alpha_1)A + (\alpha (\text{NO}_2-\text{NO}) - 1)}{(1 + \delta (\text{NO}_2))}$ against the $A$ value and use Eqs. (7) and (8) to estimate the $\alpha_2 - \alpha_1$ value (Fig. 1c). The plot shows that the best fit for the LCIE factor is $(-10 \pm 5)\%$ (root mean square error, RMSE), was lowest when $\alpha_2 - \alpha_1 = -10\%$. The uncertainties in the LCIE factor are relatively higher than that of the EIE factor, mainly because of the accumulated analytical uncertainties at low NO2 and O3 concentrations and low $A$ values (0.10–0.28) due to the relatively low $j(\text{NO}_2)$ value (1.4 × 10^{-3} s^{-1}) under the chamber irradiation conditions.

This LCIE factor determined in our experiments is in good agreement with theoretical calculations. Walters andMichalski (2016) previously used an ab initio approach to determine an $\alpha_2$ value of 0.9933 at room temperature, 0.9943 at 237 K and 0.9929 at 310 K. The total variation in $\alpha_2$ values from 273 to 310 K is only 1.4\%e, significantly smaller than our experimental uncertainty (±5\%e). The $\alpha_1$ value was calculated using a zero-point energy (ZPE) shift model (Miller andYung, 2000) to calculate the isotopic fractionation of NO2 by photolysis. Briefly, this model assumes both isotopologues have the same quantum yield function, and the PHIFE was only caused by the differences in the $^{15}\text{NO}_2$ and $^{14}\text{NO}_2$ absorption cross section as a function of wavelength; thus $\alpha_1$ values do not vary by temperature. The $^{15}\text{NO}_2$ absorption cross section was calculated by shifting the $^{14}\text{NO}_2$ absorption cross section by the $^{15}\text{NO}_2$ zero-point energy (Michalski et al., 2004). When the ZPE shift model was used with the irradiation spectrum of the chamber lights, the resulting $\alpha_1$ value was 1.0023. Therefore, the theoretically predicted $\alpha_2 - \alpha_1$ value should be $-0.0090$, i.e., $-9.0 \pm 0.7\%e$ when the temperature ranges from 273 to 310 K. This result shows excellent agreement with our experimentally determined room temperature $\alpha_2 - \alpha_1$ value of $-10 \pm 5\%e$.

This model was then used to evaluate the variations in $\alpha_1$ under different lighting conditions. The tropospheric ultraviolet and visible (TUV) radiation model (TUVS3.2; Madronich andFlocke, 1999) was used to calculate the solar wavelength spectrum at three different conditions: early morning or late afternoon (solar zenith angle = 85°), mid-morning or afternoon (solar zenith angle = 45°), and 12:00 local time (LT; solar zenith angle = 0°). These spectra were used in the ZPE shift model to calculate the $\alpha_1$ values, which are 1.0025, 1.0028 and 1.0029 at solar zenith angles of 85, 45 and 0°, respectively. These values, along with the predicted $\alpha_1$ value in the chamber, showed a total span of 0.6\%e (1.0026 ± 0.0003), which is again significantly smaller than our measured uncertainty. Therefore, we suggest that our experimentally determined LCIE factor $(-10 \pm 5)\%e$ can be used in most tropospheric solar irradiation spectra.

The equations can also be applied in tropospheric environments to calculate the combined isotopic fractionations of EIE and LCIE for NO and NO2. First, the NO2 sink reactions (mainly NO2 + OH in the daytime) are at least 2–3 orders of magnitude slower than the Leighton cycle and the NO–NO2 isotope exchange reactions (Walters et al., 2016); therefore their effects on the $\delta(\text{NO}_2)$ should be minor. Second, although the conversion of NO into NO2 in the ambient environment is also controlled by NO + NO2 and HO2 in addition to NO + O3 (e.g., King et al., 2001), Eq. (7) still showed good agreement with field observations in previous studies. Freyer et al. (1993) determined the annual average daytime $\delta(\text{NO}_2) - \delta(\text{NO})$ at Julich, Germany, along with average daytime NO concentration (9 nmol mol^{-1}, similar to our experimental conditions) to be $+18.03 \pm 0.98\%e$. Using Eq. (7), assuming the daytime average $j(\text{NO}_2)$ value throughout the year was (5.0 ± 1.0) × 10^{-3}, and a calculated $A$ value from measured NO2 concentration ranged from 0.22 to 0.33, the average NO–NO2 fractionation factor was calculated to be $+19.8 \pm 1.4\%e$ (Fig. 1c), in excellent agreement.
with the measurements in the present study. This agreement suggests that the NO + RO₂/HO₂ reactions might have similar fractionation factors as NO + O₃. Therefore, we suggest that Eqs. (7) and (8) can be used to estimate the isotopic fractionations between NO and NO₂ in the troposphere.

3.3 Calculating nitrogen isotopic fractionations of NO–NO₂

First, Eq. (7) was used to calculate the \( \Delta \text{NO}_2 – \text{NO} = \delta \text{NO}_2 – \delta \text{NO} \) at a wide range of NO₃ concentrations and \( f(\text{NO}_2) \) and \( j(\text{NO}_2) \) values (Fig. 2a–d), assuming \( 1 + \delta(\text{NO}_2) \approx 1. \) \( j(\text{NO}_2) \) values of \( 0 \text{ s}^{-1} \) (Fig. 2a), \( 1.4 \times 10^{-3} \text{ s}^{-1} \) (Fig. 2b), \( 5 \times 10^{-3} \text{ s}^{-1} \) (Fig. 2c) and \( 1 \times 10^{-2} \text{ s}^{-1} \) (Fig. 2d) were selected to represent nighttime, dawn (as well as the laboratory conditions of our experiments), daytime average and 12:00 LT, respectively. Each panel represented a fixed \( j(\text{NO}_2) \) value, and the \( \Delta \text{NO}_2 – \text{NO} \) values were calculated as a function of the A value, which was derived from NO₃ concentration and \( f(\text{NO}_2) \). The A values have a large span, from 0 to 500, depending on the \( j(\text{NO}_2) \) value and the NO concentration. When \( A = 0 \) (\( j(\text{NO}_2) = 0 \)) and \( f(\text{NO}_2) < 1 \) (meaning NO and NO₂ coexist and \( [\text{O}_3] = 0 \)), Eqs. (7) and (8) become Eqs. (2) and (3), showing that the EIE was the sole factor; the \( \Delta \text{NO}_2 – \text{NO} \) values were solely controlled by EIE, which has a constant value of \( +28.9 \%e \) at 298 K (Fig. 2a). When \( j(\text{NO}_2) > 0 \), the calculated \( \Delta \text{NO}_2 – \text{NO} \) values showed a wide range from \( -10.0 \%e \) (controlled by LCIE factor: \( \alpha_2 – \alpha_1 = -10.0 \%e \)) to \( +28.9 \%e \) (controlled by EIE factor: \( \alpha(\text{NO}_2 – \text{NO}) – 1 = +28.9 \%e \)). Figure 2b–d display the transition from an LCIE-dominated regime to an EIE-dominated regime. The LCIE-dominated regime is characterized by low \( [\text{NO}_3] \) (< 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 \( \Delta \text{NO}_2 – \text{NO} = \alpha_2 – \alpha_1 \), suggesting that the LCIE almost exclusively controls the NO–NO₂ isotopic fractionation. The \( \Delta \text{NO}_2 – \text{NO} \) values of these regions are predicted to be \( < 0 \%e \) during most times of the day and \( < -5 \%e \) at 12:00 LT. On the other hand, the EIE-dominated regime was characterized by high \( [\text{NO}_3] \) (> 20 nmol mol\(^{-1}\)) and low \( f(\text{NO}_2) \) (< 0.6), representative of regions with intensive NO emissions, e.g., near roadside or stack plumes (Clapp and 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 12:00 LT 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 \( \Delta \text{NO}_2 – \text{NO} \) values (> 20 \%). Between the two regimes, both EIE and LCIE are competitive, and therefore it is necessary to use Eq. (7) to quantify the \( \Delta \text{NO}_2 – \text{NO} \) values.

Figure 2 also implies that changes in the \( j(\text{NO}_2) \) value can cause the diurnal variations in \( \Delta \text{NO}_2 – \text{NO} \) values. Changing \( j(\text{NO}_2) \) would affect the value of A and consequently the NO–NO₂ isotopic fractionations in two ways: (1) changes in the \( j(\text{NO}_2) \) value would change the photolysis intensity and therefore the \( \tau_{\text{photo}} \) value; (2) in addition, changes in the \( j(\text{NO}_2) \) 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 NO₃ concentration data and atmospheric chemistry models.

We then calculated the differences in \( \delta^{15} \text{N} \) values between NO₂ and total NO₃, e.g., \( \Delta \text{NO}_2 – \text{NO}_x = \delta \text{NO}_2 – \delta \text{NO}_x \) in Fig. 2e–h. Since \( \Delta \text{NO}_2 – \text{NO}_x \) are connected through the observed \( \delta^{15} \text{N} \) of NO₂ (or nitrate) to the \( \delta^{15} \text{N} \) of NO₃ sources, this term might be useful in field studies (e.g., Chang et al., 2018; Zong et al., 2017). The calculated \( \Delta \text{NO}_2 – \text{NO}_x \) values (Fig. 2e–h) also showed an LCIE-dominated regime at low \( [\text{NO}_3] \) and an EIE-dominated regime at high \( [\text{NO}_3] \). The \( \Delta \text{NO}_2 – \text{NO}_x \) values were dampened by the \( 1 – f(\text{NO}_2) \) factor comparing to \( \Delta \text{NO}_2 – \text{NO} \), as shown in Eqs. (3) and (8): \( \Delta \text{NO}_2 – \text{NO}_x = \Delta \text{NO}_2 – \text{NO} \) (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 \( \delta(\text{NO}_x) \) values were similar to \( \delta(\text{NO}_2) \), although the isotopic fractionation between NO and NO₂ could be noteworthy. Some ambient environments with significant NO emissions or high NO₂ photolysis rates usually have \( f(\text{NO}_2) \) values between 0.4 and 0.8 (Mazzeo et al., 2005; Vicars et al., 2013). In this scenario, the \( \Delta \text{NO}_2 – \text{NO}_x \) values in Fig. 2f–h showed wide ranges of \( -4.8 \%e \) to \( +15.6 \%e \), \( -6.0 \%e \) to \( +15.0 \%e \) and \( -6.3 \%e \) to \( +14.2 \%e \) at \( j(\text{NO}_2) = 1.4 \times 10^{-3}, 5 \times 10^{-3} \text{ and } 1 \times 10^{-2} \text{ s}^{-1} \), respectively. These significant differences again highlighted the importance of both LCIE and EIE (Eqs. 7 and 8) in calculating the \( \Delta \text{NO}_2 – \text{NO}_x \). In the following discussion, we assume that (1) the \( \alpha_1 \) value remains constant (see discussion above), (2) the NO + RO₂/HO₂ reactions have the same fractionation factors (\( \alpha_2 \) as NO + O₃), and (3) both EIE and LCIE do not display significant temperature dependence. We then use Eqs. (7) and (8) and this laboratory-determined LCIE factor (–10 \%) to calculate the nitrogen isotopic fractionation between NO and NO₂ at various tropospheric atmospheric conditions.

4 Implications

The daily variations in \( \Delta \text{NO}_2 – \text{NO}_x \) values at two roadside NO₃ monitoring sites were predicted to demonstrate the effects of NO₃ concentrations to the NO–NO₂ isotopic fractionations. Hourly NO and NO₂ concentrations were acquired from a roadside site at Anaheim, CA (https://www.arb.ca.gov, last access: 9 August 2019), and an urban site at Evansville, IN (http://idem.tx.sutron.com, last access: 9 August 2019), on 25 July 2018. The hourly \( j(\text{NO}_2) \) values output from the TUV model (Madronich and Flocke, 1999) at these locations were used to calculate the daily variations.
in $\Delta(\text{NO}_2-\text{NO}_x)$ values (Fig. 3a, b) by applying Eq. (8) and assuming $1 + \delta(\text{NO}_2) \approx 1$. Hourly NO$_x$ concentrations were 12–51 nmol mol$^{-1}$ at Evansville 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 NO$_x$ concentrations were controlled by the high NO emissions from the road (Gao, 2007). The calculated $\Delta(\text{NO}_2-\text{NO}_x)$ values using Eq. (8) showed significant diurnal variations. During the nighttime, the isotopic fractionations were solely controlled by the EIE; the predicted $\Delta(\text{NO}_2-\text{NO}_x)$ 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 predicted $\Delta(\text{NO}_2-\text{NO}_x)$ 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 $\Delta(\text{NO}_2-\text{NO}_x)$ values for both sites (+7.0‰ and +1.7‰) occurred around 12:00 LT, when the NO$_x$ photolysis was the most intense. In contrast, if one neglects the LCIE factor in the daytime, the $\Delta(\text{NO}_2-\text{NO}_x)$ values would be +12.9 ± 1.5‰ and +10.0 ± 1.6‰, respectively, an overestimation of 3.1‰ and 6.9‰. These discrepancies suggested that the LCIE played an important role in the NO$_x$-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. The $\Delta(\text{NO}_2-\text{NO}_x)$ values were calculated for a suburban site near San Diego, CA, USA, again using the hourly NO$_x$ concentrations (https://www.arb.ca.gov; Fig. 3c) and $f(\text{NO}_2)$ values calculated from the TUV model. NO$_x$ concentrations at this site varied from 1 to 9 nmol mol$^{-1}$, assuming $1 + \delta(\text{NO}_2) \approx 1$. During the nighttime, NO$_x$ was in the form of NO$_2$ ($f(\text{NO}_2) = 1$) because O$_3$ concentrations were higher than NO$_x$; thus the $\delta(\text{NO}_2)$ values should be identical to $\delta(\text{NO}_x)$ ($\Delta(\text{NO}_2-\text{NO}_x) = 0$). In the daytime a certain amount of NO was produced by direct NO emission and NO$_2$ photolysis, but the $f(\text{NO}_2)$ was still high (0.73 ± 0.08). Our calculation suggested that the daytime $\Delta(\text{NO}_2-\text{NO}_x)$ values should be only +1.3±3.2‰, with a lowest value of −1.3‰. These $\Delta(\text{NO}_2-\text{NO}_x)$ values were similar to the observed and modeled summer daytime $\delta(\text{NO}_2)$ values in West Lafayette, IN (Walters et al., 2018), which suggest that the average daytime $\Delta(\text{NO}_2-\text{NO}_x)$ 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 that the $\Delta(\text{NO}_2-\text{NO}_x)$ values were generally small due to the significant contribution of LCIE and high $f(\text{NO}_2)$. 

The LCIE should be the dominant factor controlling the NO–NO$_x$ isotopic fractionation in remote regions, resulting in a completely different diurnal pattern of $\Delta(\text{NO}_2-\text{NO}_x)$ compared with the urban–suburban area. Direct hourly measurements of NO$_x$ at remote sites are rare; thus we used a total NO$_x$ concentration of 50 pmol mol$^{-1}$ and a 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 $1 + \delta(\text{NO}_2) \approx 1$ and that the conversion of NO to NO$_2$ was completely controlled by O$_3$ to calculate the NO/NO$_2$ ratios. Here the isotopes of NO$_x$ were almost exclusively controlled by the LCIE due to the high $A$ values (≈ 110). The $\Delta(\text{NO}_2-\text{NO}_x)$ values displayed a clear diurnal pattern (Fig. 3d), with a maximum value of −0.3‰ in the “nighttime” (solar zenith angle > 85°) and a minimum value of −5.0‰ during midday. This suggests that the isotopic fractionations between NO and NO$_2$ were almost completely controlled by LCIE in remote regions when NO$_x$ concentrations were < 0.1 nmol mol$^{-1}$. However, since the isotopic fractionation factors of nitrate formation reactions (NO$_2$ + OH, NO$_3$ + HC, N$_2$O$_5$ + H$_2$O) are still unknown, more studies are needed to fully explain the daily and seasonal variations in $\delta(\text{NO}_3)$ in remote regions.

Figure 2. Calculating isotopic fractionation values between NO–NO$_2$ ($\Delta(\text{NO}_2-\text{NO})$; a–d) and NO$_x$–NO$_2$ ($\Delta(\text{NO}_2-\text{NO}_x)$; e–h) at various $j(\text{NO}_2)$, NO$_x$ level and $f(\text{NO}_2)$ using Eqs. (7) and (8). Each panel represents a fixed $j(\text{NO}_2)$ value (on the upper-right side of each panel), and the fractionation values are shown by color. Lines are contours with the same fractionation values at an interval of 5‰; the contour line representing 0‰ was marked in each panel except for panels (a) and (e).
Nevertheless, our results have a few limitations. First, currently there are very few field observations that can be used to evaluate our model; therefore, future field observations that measure the $\delta^{15}$N values of ambient NO and NO$_2$ should be carried out to test our model. Second, more work, including theoretical and experimental studies, is needed to investigate the isotope fractionation factors occurring during the conversion from NO$_x$ to NO$_y$ and nitrate; in the NO$_y$ cycle, EIE (isotopic exchange between NO$_2$, NO$_3$ and N$_2$O$_5$), KIE (formation of NO$_3$, N$_2$O$_5$ and nitrate) and PHIFE (photolysis of NO$_3$, N$_2$O$_5$, HONO and sometimes nitrate) may also exist and be relevant for the $\delta^{15}$N of HNO$_3$ and HONO. In particular, the N isotope fractionation occurring during the NO$_2$ + OH $\rightarrow$ HNO$_3$ reaction needs investigation. Such studies could help us to model the isotopic fractionation between NO$_x$ emission and nitrate and eventually enable us to analyze the $\delta^{15}$N value of NO$_x$ emission by measuring the $\delta^{15}$N values of nitrate aerosols and nitrate in wet depositions. Third, our discussion only focuses on the reactive nitrogen chemistry in the troposphere; however, the nitrogen chemistry in the stratosphere is drastically different from the tropospheric chemistry; thus future studies are also needed to investigate the isotopic fractionations in the stratospheric nitrogen chemistry. Last, the temperature dependence of both EIE and LCIE needs to be carefully investigated because of the wide range of temperature in both the troposphere and stratosphere. Changes in temperature could alter the isotopic fractionation factors of both EIE and LCIE as well as contribute to the seasonality of isotopic fractionations between NO$_x$ and NO$_y$ molecules.

5 Conclusions
The effect of NO$_x$ photochemistry on the nitrogen isotopic fractionations between NO and NO$_2$ was investigated. We first measured the isotopic fractionations between NO and NO$_2$ and provided mathematical solutions to assess the impact of NO$_x$ level and NO$_2$ photolysis rate ($j$(NO$_2$)) on the relative importance of EIE and LCIE. The EIE and LCIE isotope fractionation factors at room temperature were determined to be 1.0289 $\pm$ 0.0019 and 0.990 $\pm$ 0.005, respectively. These calculations and measurements can be used to determine the steady-state $\Delta$(NO$_2$–NO) and $\Delta$(NO$_2$–NO$_x$) values at room temperature. Subsequently we applied our equations to polluted, clean and remote sites to model the daily variations in $\Delta$(NO$_2$–NO$_x$) values. We found that the $\Delta$(NO$_2$–NO$_x$) values could vary from over +20% to less than $-5\%$ depending on the environment: in general, the role of LCIE becomes more important at low NO$_x$ concentrations, which tend to decrease the $\Delta$(NO$_2$–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 tropospheric environments, which could help interpret the measured $\delta^{15}$N values of NO$_2$ and nitrate in field observation studies.

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Appendix A: Chamber descriptions

The chamber is a 10 m$^3$ Teflon bag equipped with several standard instruments including a temperature and humidity probe, NO$_x$ monitor and O$_3$ monitor. A total of 128 wall-mounted blacklight tubes surrounded the chamber to mimic tropospheric photochemistry, and the photolysis rate of NO$_2$ ($j$(NO$_2$)) when all lights are on has been previously determined to be 1.4 $\times$ 10$^{-3}$ s$^{-1}$, similar to a $j$(NO$_2$) coefficient at an 81$^\circ$ solar zenith angle. The irradiation spectrum of the black lights is shown in Fig. A1. The chamber was kept at room temperature and 1 atm. Before each experiment, the chamber was flushed with zero air at 40 L min$^{-1}$ for at least 12 h to ensure the background NO$_x$, O$_3$ and other trace gases were below the detection limit.

Figure A1. Spectral actinic flux versus wavelengths of the UV light source used in our experiments.

Appendix B: Box model assessing the time needed for NO–NO$_2$ to reach isotopic equilibrium

The time needed to reach NO–NO$_2$ isotopic equilibrium during light-off experiments was assessed using a 0-D box model. This box model contains only two reactions:

\begin{align}
15\text{NO}_2 + ^{14}\text{NO} & \rightarrow 15\text{NO} + ^{14}\text{NO}_2 \\
k &= 8.14000 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \quad \text{(BR1)} \\
15\text{NO} + ^{14}\text{NO}_2 & \rightarrow 15\text{NO}_2 + ^{14}\text{NO} \\
k' &= 8.37525 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1.} \quad \text{(BR2)}
\end{align}

where $k$ and $k'$ are rate constants of the reactions. The differences in rate constants were calculated by assuming an $\alpha$(NO$_2$–NO) value of 1.0289. Six simulations were conducted at various initial NO (with $\delta^{15}$N = 0‰) and O$_3$ levels that were similar to our experiment. Then the $\delta^{15}$N values of NO and NO$_2$ during the simulation were calculated from the model and are shown in Fig. B1, suggesting that in our experimental condition, all systems should reach isotopic equilibrium within 1 h.
Figure B1. Simulated NO–NO\textsubscript{2} isotopic equilibrium process in the chamber at various NO and O\textsubscript{3} concentrations.
Appendix C: Deriving Eqs. (7) and (8)

When the system (Reactions R1–R6) reaches a steady state, we have
\[ \frac{d[^{15}\text{NO}_2]}{dt} = 0. \]  
(C1)

Therefore, using Reactions (R1)–(R6)
\[ k_1[^{15}\text{NO}_2][^{14}\text{NO}] + j(\text{NO}_2)\alpha_1[^{15}\text{NO}_2] = k_3\alpha_2[^{15}\text{NO}][\text{O}_3] + k_1\alpha(\text{NO}_2–\text{NO})[^{15}\text{NO}][^{14}\text{NO}]. \]  
(C2)

From here we refer to $^{14}\text{NO}_2$ and $^{14}\text{NO}$ as NO$_2$ and NO for convenience. Rearranging the above equation, we get
\[ \frac{[^{15}\text{NO}_2]}{[^{15}\text{NO}]} = \frac{k_3\alpha_2[\text{O}_3] + k_1\alpha(\text{NO}_2–\text{NO})[\text{NO}_2]}{j\text{NO}_2\alpha_1 + k_1[\text{NO}]} . \]  
(C3)

Meanwhile, since the Leighton cycle reaction still holds for the majority of isotopes (NO and NO$_2$), we have
\[ j\text{NO}_2[\text{NO}_2] = k_5[\text{NO}][\text{O}_3]. \]  
(C4)

Thus,
\[ \frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k_5 \times [\text{O}_3]}{j\text{NO}_2} . \]  
(C5)

From the text, when $j\text{NO}_2 > 0$, we defined $A = r_\text{exchange}/r_\text{photo} = j\text{NO}_2/(k_1 \times [\text{NO}])$. Using the above equations, we know
\[ \frac{j\text{NO}_2}{[\text{NO}_2]} = \frac{k_5[\text{O}_3]}{[\text{NO}_2]} = A k_1 \]  
(C6)

\[ \frac{j\text{NO}_2}{k_1[\text{NO}]} = \frac{k_5[\text{O}_3]}{k_1[\text{NO}_2]} = A . \]  
(C7)

Next, to calculate $\delta(\text{NO}_2)–\delta(\text{NO})$, we use the definition of delta notation:
\[ \delta(\text{NO}_2)–\delta(\text{NO}) = R_{\text{NO}_2}/R_{\text{SD}} – R_{\text{NO}}/R_{\text{SD}} \]
\[ = (R_{\text{NO}_2}/R_{\text{NO}} - 1)(1 + \delta(\text{NO})) \]  
(C8)

\[ \frac{R_{\text{NO}_2}}{R_{\text{NO}}} = \frac{[^{15}\text{NO}_2][\text{NO}]}{[^{15}\text{NO}][\text{NO}_2]} \]
\[ = \frac{k_3\alpha_2[\text{O}_3][\text{NO}] + k_1\alpha(\text{NO}_2–\text{NO})[\text{NO}_2][\text{NO}]}{j\text{NO}_2\alpha_1[\text{NO}_2] + k_1[\text{NO}][\text{NO}_2]} . \]  
(C9)

Divide both sides by $k_1[\text{NO}][\text{NO}_2]$: 
\[ \frac{R_{\text{NO}_2}}{R_{\text{NO}}} = \frac{k_3\alpha_2[\text{O}_3]}{k_1[\text{NO}_2]} + \alpha(\text{NO}_2–\text{NO}) \]
\[ = \frac{j\text{NO}_2\alpha_1}{k_1[\text{NO}]} + 1 . \]  
(C10)

Rearrange and substitute $\frac{k_5[\text{O}_3]}{k_1[\text{NO}_2]}$ and $\frac{j\text{NO}_2}{k_1[\text{NO}]}$ with A:
\[ \frac{R_{\text{NO}_2}}{R_{\text{NO}}} = \frac{\alpha_2 A + \alpha(\text{NO}_2–\text{NO})}{\alpha_1 A + 1} . \]  
(C11)

\[ \frac{R_{\text{NO}_2}}{R_{\text{NO}}} = \frac{\alpha_2 A + \alpha(\text{NO}_2–\text{NO})}{\alpha_1 A + 1} . \]  
(C12)

\[ \frac{R_{\text{NO}_2}}{R_{\text{NO}}} = \frac{(\alpha_1 - \alpha_2) A - (\alpha(\text{NO}_2–\text{NO}) - 1)}{\alpha_1 A + \alpha(\text{NO}_2–\text{NO})} . \]  
(C13)

Thus,
\[ \delta(\text{NO}_2)–\delta(\text{NO}) = \frac{(\alpha_1 - \alpha_2) A - (\alpha(\text{NO}_2–\text{NO}) - 1)}{\alpha_1 A + \alpha(\text{NO}_2–\text{NO})} + (1 + \delta(\text{NO}_2)). \]  
(C14)

Then, using mass balance
\[ \delta(\text{NO}_2) f(\text{NO}_2) + \delta(\text{NO})(1 - f(\text{NO}_2)) = \delta(\text{NO}_x) . \]  
(C15)

we can derive Eq. (8):
\[ \delta(\text{NO}_2)–\delta(\text{NO}_x) = \frac{(\alpha_2 - \alpha_1) A + \alpha(\text{NO}_2–\text{NO}) - 1}{\alpha_1 A + \alpha(\text{NO}_2–\text{NO})} \]
\[ (1 + \delta(\text{NO}_2))(1 - f(\text{NO}_2)). \]  
(C16)
Data availability. Data acquired from this study were deposited at Open Sciences Framework (Li, 2019; https://doi.org/10.17605/OSF.IO/JW8HU).

Author contributions. JL and GM designed the experiments, XZ and JL conducted the experiments. XZ, GM, JO and GT helped JL in interpreting the results. The manuscript was written by JL, and all the authors have contributed during the revision of the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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