Response to RC1

Dear Dr. Johnson,

Thank you for the comments and input to our manuscript. Below is a line-by-line response to your comments.

Model and Interpretation

The semi-analytical PHIFE/ZPE model (Miller 2000; Michalski 2004) is discussed as a way of understanding photolytic isotopic fractionation. Please compare the predictions of that theory with the results of this experiment and comment.

We discussed the previous calculation of the KIE and added some theoretical calculations in our manuscript. The predictions showed good agreement with our observation (KIE=0.9933, PHIFE=1.0023, therefore predicted LCIE=-9‰, our results=-10±5‰). In the meantime, we did the ZPE calculation using 4 different actinic flux spectrums (lab light, early morning/late afternoon, mid-morning/afternoon, and noon), all of them showed similar PHIFE values ranging from 1.0023 to 1.0029, suggesting the PHIFE do not vary significantly by light.

The abstract states that the Leighton cycle isotope effect is 0.990 ± 0.005 at room temperature. However, this must be for a certain insolation spectrum and concentrations of O3, HO2, RO2? Please include the conditions. How much will the LCIE change with the changes in conditions found in the atmosphere, or can we take this result to be applicable throughout the atmosphere?

We pointed out that, our experiments measured the LCIE fractionation factor when O_3 solely controls the NO_x cycle. However, we suggest this LCIE factor might be used in the ambient environment because it showed good agreement with previous field observations. Nevertheless, future work is needed to confirm our assumption that the isotopic fractionation factor of $NO+RO_2/HO_2$ are similar to that of $NO+O_3$.

It is argued that the atmospheric LCIE is 18.8 per mil based on the experiment and one field measurement. This may perhaps be sufficient for accepting the proposed value, but no attempt is made to discuss the uncertainty of the measurement, and to predict what variations will be seen in the atmosphere with changes in temperature, actinic flux spectrum, and concentrations of O3, HO2, and RO2. Please present a discussion of these factors.

This 18.8 ‰ value in Freyer's work is an annual average daytime value of combined EIE and LCIE, which was determined using all the measurements in a year. In reality, the value significantly varies by temperature, actinic flux spectrum, and concentrations of O_3, HO_2, and RO_2. However, since we do not have more detailed data, we are not able to reconstruct the combined LCIE+EIE values at a higher time resolution in Freyer's work. Instead, we discussed this variation in the next section by using hourly NO, NO_2 and j(NO_2) data to model the daily variations.

What affect will the formation of PANs/addition of this equilibrium, have on the LCIE? Please comment on the LCIE that would be observed in the stratosphere.

This is a very good point. However, since 1) reactive nitrogen chemistry in the stratosphere is dramatically different from the troposphere and 2) the temperature in the stratosphere is also different, we suggest our model may not be used in the stratosphere. Therefore, we revised our statement and limited our discussion in the troposphere. In the meantime, we pointed out that future study is needed to explore the behavior of N isotopes in the stratosphere.

In the authors' experiment, NO is converted to NO2 by O3 in conditions with low concentrations of HO2 and RO2, which will play a role in the atmosphere. They suggest that the HO2 and RO2 oxidations of NO might have a similar KIE as the O3 oxidation, but this argument could be considered convenient. It would be stronger with experimental evidence and with improved validation by field measurements. Please make sure to discuss the potential uncertainty that is being introduced in transferring the laboratory results to the field.

We addressed this uncertainty by mentioning that, to enable our model in the ambient environment, we assume the KIE of O_3 is similar to that of HO_2 and RO_2, because our modelled KIE value could explain the only field observation data by Freyer. This is an assumption that needs to be verified in the future.

However, if this assumption is true, then we do not need to know the concentrations of O_3, HO_2 or RO_2, if we know both NO and NO_2 concentrations. The existence of O_3, HO_2 or RO_2 would be reflected in the NO/NO_2 ratio at a given j(NO_2) value.

No description is made of the UV lights that were used for the photolysis, please add this. According to PHIFE/ZPE, photolytic isotopic fractionation changes as a function of wavelength. How did the spectrum of the lamps used to differ from the solar actinic flux spectrum? What wavelength dependence do you expect? How will the LCIE change as a function of altitude in the atmosphere as the actinic flux spectrum changes?

We added the description of the UV light in the supplementary material. And as mentioned before, we studied the variation of LCIE by calculating the PHIFE using 4 different actinic flux spectrums (lab light, early morning/late afternoon, mid-morning/afternoon, and noon). The results show that all of them have similar PHIFE values ranging from 1.0023 to 1.0029, suggesting the PHIFE do not vary significantly under different actinic flux spectrums.

There is precious little field data to use to validate the model. Please comment on what studies you would like to see in order to test the model, and as I have noted, please discuss the impact of different environmental factors, other than NOx concentration, on the results.

We added a paragraph before the final conclusion discussing the limitations of our work and potential future work that can be done to advance our understanding in this topic.

Presentation:

The abstract is rather short given the interesting findings of the paper. Please expand.

Revised as suggested. We rewrote the abstract to make it readable for a more general audience.

I am not sure why the TLA (three letter acronym) 'EIE' for 'equilibrium isotope effect' is introduced when there is already the widely accepted idea of the exchange reaction. This could make the abstract obscure for non-specialists.

Revised as suggested. We removed the TLA for EIE in the abstract but remained using EIE in the main text to contrast with LCIE.

The introduction should include discussion of photolytic re-emission of deposited nitrate.

Revised as suggested.

Please italicize the symbols used for physical quantities such as f, j and k.

Revised as suggested.

Please add a scheme or figure giving an overview of the key reactions involved in this work.

We added a sketch as Fig. 1C.

On page 11 line 230, some j values (photolysis rates) are presented. Please include the units with these numbers. Also, in figure 2, 'j = 0.005', but what are the units?

Revised as suggested.

Response to RC2

Dear reviewer:

Thank you for the comments, we appreciate your input. We have revised our manuscript according to the comments from all the reviewers, below is our line-by-line response to your comments and suggestions.

First and foremost, how was the d15N of NOx measured (lines 150-151)? This is critical in that these values are used to demonstrate and calculate the observed isotope effects.

We improved our description of measuring the $\delta^{15}N$ of NO_x in the method section. In short, we measured the $\delta^{15}N$ of NO_x in three different experiments. In each experiment, we inject same amount of NO and O_3 to produce pure NO_2, then we analyze the $\delta^{15}N$ value of the NO_2. Because we can see that 100% of NO_x in these experiments were in the form of NO_2, therefore the measured $\delta^{15}N$ value can be used to represent the $\delta^{15}N$ of source NO_x.

Second, was the d15N data of all samples corrected for potential isobaric in- fluences of 17O? (lines 120-124). The generated O3 should have a high D17O that will be transferred to the product NO2. This may impact both the starting NO source d15N values and the measured NO2 values during both dark and photochemical experiments. This could cause an important change in the findings if excess 17O has not been accounted for in correcting the d15N data. Related to the above, in Figure 1A it appears that the data was forced through an intercept of 0. But the best fit to the data does not appear to go through 0. What is the slope of the data not forced through the intercept? What might the intercept indicate – from my read this could indicate a shift due to the influence of 17O on the 45 signals when quantifying the isotopic ratios from N2O. A change in slope with the best fit might also bring the calculated value to something that is actually closer to the measured value by Walters et al. Wouldn't this be more consistent with current thinking?

The isobaric influence of O17 was calculated in the ISODAT system. It measures the 46 signals to calculate $\delta^{18}O$ first, then calculate the $\delta^{17}O$ value assuming mass dependent fractionation, then use these to correct for $\delta^{15}N$ signal. We notice that this method did not account for mass independent fractionation so it could shift the absolute $\delta^{15}N$ value (assuming O17 excess=30‰) by as much as 1.5‰.

However, all the data shown on Figure 1A are $\delta(NO_2)$-$\delta(NO_x)$, and both $\delta(NO_2)$ and $\delta(NO_x)$ have the same isobaric shift because they were measured using the same sampling & analysis method. So, when calculating the $\delta(NO_2)$-$\delta(NO_x)$ values, this isobaric error should be cancelled out assuming O17 excess were the same. Therefore, the isobaric error may not cause a significant shift in the interception on Figure 1A.

In other words, our experiments that determined the $\delta^{15}N$ values of source NO_x (in these experiments f(NO)=0 and $\delta(NO_2)$-$\delta(NO_x)$=0) can be seen as 3 extra data points at (0,0), therefore the interception on Figure 1A should still be 0.

For Figure 1B, the LCIE factor is calculated from "the best fit" (line 206). However, the figure makes it appear qualitative rather than quantitative. This calculation/estimation should be shown quantitatively and an r or r2 value should be reported for the fit. It should also be better explained why the point at A~0.1 and A~0.15 do not follow the expected relationship (why does the difference in d15N not change with A?). Also, why does the relationship have to be linear? In addition, the -10 per mil line does not "best fit" the field observation. It is also not clear what the error bars are on each symbol – I don't see how these should be the same/have the same meaning for the field observation versus the chamber data. The field study point should also be clearly cited in the figure caption. Related to this, in the text (line 215-218) it is argued that the experimental values determined are in good agreement with the field study. But the field study represents a very high NOx environment (at times NOx » O3) and the measurements were taken at different times of the year not just at temperature close to room temperature. So, is it possible that the field determined value is showing a temperature dependence relative to the controlled experiments?

We call the -10‰ LCIE line "best fit" because this fit gives the highest r value of 0.52 and the lowest total variation:

total variation=$\sum(y_i - f_i)^2$

in which y_i is the observed value and f_i is the predicted value by the fit line.

We attribute the deviation of the two points from the prediction line to the relatively large analytical uncertainties at low A values. In these two experiments, the NO and NO_2 level were low (<10 ppb), and the concentration measurements showed a higher error bar. We have recalculated the error bars on these data points which are now shown on Figure 1B.

We used the average conditions of the field study to calculate its position at Figure 2B. Although the conditions change significantly throughout the time period of this study, their 18.8‰ value represented the average fractionation factor of the sampling period. Therefore, we also used their average condition to calculate the fractionation factor. However, it is likely that the temperature dependence played a role in this study, and we pointed out that future studies are needed to investigate its impact.

Next, how does the EIE measurement compare with theoretical works? What may drive the differences in the experimental values versus theory? Is formation of other products (such as N2O3 or N2O4) in the chamber a concern and could that influence the measured EIE value?

We added some calculations showing the formation of N_2O_4 and N_2O_3 were negligible. Also, we have mentioned that we conducted a control experiment to evaluate NO_2 wall loss but did not observe any NO_2 loss over a 4-hour period. Therefore, we suggest the formation of other products were insignificant.

We are not sure why it did not align with current theoretical calculations, probably because of the different approximation methods in previous studies. Hopefully future theoretical calculations can be carried out to evaluate our conclusions.

On line 185-189, it is stated that a2 ("alpha 2") is not quantified. However, Walters and Michalski (2016), which is referenced here, does include an ab initio-based estimate for this value. And couldn't this value be used to separate out the magnitude of PHIFE (rather than assume it)?

We added two paragraphs comparing our results to theoretical calculations. We pointed out that our result of -10‰ showed good agreement with theoretical calculations in Walters and Michalski (2016) and a ZPE approach that estimates the isotopic fractionation of NO_2 photolysis.

Specific comments: Abstract – The abstract should be written for a more general audience. Be consistent with abbreviations. For example, NO and NO2 are not defined and nitrate isn't abbreviated. Also, LCIE should be more clearly defined since this is new terminology in this work. The implications of the study should be better highlighted here. How will a mathematic solution for NO-NO2 isotopic fractionation be useful to the atmospheric chemistry community?

We have revised our abstract, defined NO, NO_2 and introduced LCIE. We also revised our implication and pointed out the limitation of this study.

Also, the statement that the new solution can be used at any given condition is a stretch since experiments were only conducted at room temperature and the experiments seem to be most relevant for the troposphere and not stratospheric NOx conditions.

We realized our experimentally determined values have limitations; therefore, we have discussed these limitations, and suggested our result should be applied in troposphere near room temperature. We also discussed how can future work verify and improve our current results.

Main Text

Line 25-30: The link between NOx and the formation of nitric acid (i.e. nitrate) needs to be more clearly stated. Also, the second sentence is a bit awkwardly phrased given that most of the studies did not use NO2 isotopes directly. It may be worth separating out the studies that have used isotopes of nitrate to understand something about NOx versus studies that have looked at NO2 or NOx specifically.

We revised the first paragraph. We now start this introduction by stating that the N isotopes are usually applied to study the sources of nitrate, however, it is unclear how atmospheric chemistry alters the isotope signals. Then, we narrow down our topic to the isotopic fractionations between NO and NO_2, because it is very important.

Line 38: remove "the" before chemistry

Revised as recommended.

Lines 46-54: Please separate this into at least two separate sentences.

Revised as recommended.

Lines 61-63: What drives the difference in the theoretical predictions for this EIE?

It is mainly because each theoretical prediction uses different harmonic approximations in their calculation.

Lines 63-64: I think it should be pointed out that this was conducted at room temperatures. Also, the error of ±0.001 is incorrect?

Revised as recommended.

Lines 68-69: KIE and PHIFE for the NOx system is limited but you should probably acknowledge the KIE study on NO + O3: Walters and Michalski (2016) Ab initio study of nitrogen and position-specific oxygen kinetic isotope effects in the NO + O3 reaction, J. Chem. Phys. 145, 224307.

Revised as recommended.

Lines 70-75: suggest changing this to ". . .tends to diminish the expression of the equilibrium isotopic fractionation (EIE) between NO and NO2, but both KIE and PHIFE factors at that time were unknown." It seems strange to suggest that assuming no isotope effects (ie 1) yields no isotope effect. Here would be a good place to better detail the Freyer et al work and approach to determining the single fractionation factor. Otherwise line 75 doesn't really make sense to the reader unfamiliar with the details of Freyer's work.

We have revised this part to present a better description of Freyer's work and pointed out the limitation, which is the motivation of our study.

Line 83: atmospheric should be "atmospherically"

Revised as recommended.

Line 88: change "NOx nitrogen isotopes" to something more correct like isotopic composition of NOx.

Revised as recommended.

Line 105: "was" should be were. Line 105 (and later): what range of wavelengths are used in the experiment. This is important to report as you have already stated!

Revised as recommended.

Lines 112-115: More details on the capture of NO using denuder tubes should be provided in the text rather than supplement. And the details are not really given in the suppl either. What was the denuder coated with? How is it determined that there was quantitative and accurate collection of the NO isotopes? What is this method based upon?

Revised as recommended.

Lines 120-124: Were corrections conducted for D17O interferences? I imagine the generated O3 will have a high D17O that will be proportional transferred to your product NO2. This may impact both your starting NO source d15N value and your measured NO2 values during dark and photochemical experiments. Section 2 overall – were any blanks tested throughout the experiments?

The D17O will affect the measured absolute δ^{15}N values but this should be cancelled out when we calculate the $\delta(NO_2)$-$\delta(NO_x)$ values (see our reply above). We tested 6 blanks during our experiments and none of them showing any measurable nitrite. We have added this part into the main text.

Line 129: difference should be “ratio of” correct?

Revised as recommended.

Line 140: I don’t understand the formatting here with d(15N, NO)?

We changed this notation to $\delta^{15}N(NO)$.

Line 149- 150: How was d15N-NOx measured? If this was done for all experiments, why does n=3? and again how will potential 17O isobaric influences affect your quantification of d15N?

As we described above, three extra experiments have been conducted in which we convert all the NO into NO_2 and measured the $\delta^{15}N$ values of NO_2 to represent the $\delta^{15}N$ of NO_x. All three experiments showed consistent $\delta^{15}N$ values, therefore we suggest the $\delta^{15}N$ value of NO_x remain the same in all of our experiments.

Lines 156: Where does the error on the 26.8 value come from? This is not represented in the figure.

Since the slope actually represents the $\delta(NO_2)$-$\delta(NO)$ values in each experiment, we calculated the error using the standard deviations of $\delta(NO_2)$-$\delta(NO)$ values in the 5 experiments.

Lines 166-167: Can you prove that formation of these other products are not important for the experiments performed here? EIE should be able to be precisely predicted by theory – so why is there such a mismatch between the theoretical and the measured values?

We added some calculations showing the formation of N_2O_4 and N_2O_3 were negligible. Also, we have mentioned that we conducted a control experiment to evaluate NO_2 wall loss but did not observe any NO_2 loss over a 4-hour period. Therefore, we suggest the formation of other products were insignificant.

We are not sure why it did not align with current theoretical calculations, probably because of the different approximation methods in previous studies. We suggest that future theoretical calculations can be carried out to evaluate our conclusions.

Figure 1A: It appears that the data was fitted through an intercept of 0, but the data doesn’t appear to go through the intercept. What is the slope of the data when not forced through the intercept? What might the intercept of your data indicate? Maybe D17O isobaric influence?

Since the $\delta(NO_x)$ is determined using the same method as $\delta(NO_2)$ in our experiments, this isobaric influence in this equation should be cancelled out (see our reply above). Therefore, this slope should have an intercept of 0.

Lines 174-176: What exactly were the wavelengths of the blacklight used in the experiments?

We provided an irradiation spectrum of the UV light we used in the supplementary material.

Lines 186-189: α2 value was determined in Walters and Michalski, 2016 ab initio study as referenced above.

We changed the statement to "nor were α1 and α2 experimentally determined"

Lines 191-197: It might be more straightforward if t(exchange) and t(photo) were defined first and then A, etc. Also please better define the purpose of equations 7 and 8. Also shouldn't these equations have epsilon instead of alpha?

Revised as recommended. In these calculations, since ε=(α-1)*1000‰, we know ε2-ε1=(α2-α1)*1000‰. To introduce as little symbols as possible, we did not use ε in this section.

Line 207-210: The experimental LCIE should be compared with the NO + O3 KIE. Here and on line 225 it feels a bit like the large uncertainty of +/- 50 percent on the -10 value is being ignored!

We added some extra discussion suggesting 1) this -10‰ value fits well with theoretical predictions and 2) the α_1 value did not vary significantly with a changing $j(NO_2)$. Therefore, we will use this -10‰ in the following discussion assuming the α_1 value remain constant, and 2) the $NO+RO_2/HO_2$ reactions have the same fractionation factors (α_2) as $NO+O_3$.

Line 220: Note that the field experiments sometimes only represent NO2 and other times NOx. . .so the difference between NO and NO2 was not measured, it was determined.

Revised as recommended.

Line 237: I do not see how this shown in Figure 2A.

Figure 2A represents the isotopic fractionations between NO and NO_2 in dark condition ($j(NO_2)=0$). In this scenario, EIE solely controls the isotopic fractionation therefore the $\delta(NO_2)$-$\delta(NO)$ should be a constant no matter how NO_x level and f(NO2) changes.

Line 261-263: These are not emissions, these are ambient NO2 and NOx. Also, NOx is not emitted – primary emissions are NO and very on occasion diesel engines have been shown to emit NO2 directly. All of the language here needs to be much more precise.

We changed "NO_x emission" to "total NO_x".

Section 4 overall: This section needs work. It needs to be established why the sites were chosen. And the sites should be clearly labeled as representative of, for instance, urban versus suburban versus remote versus elevated NOx (roadside) or the like. It seems like the point here actually should be to distinguish the effects across the different sites. Why does it not matter that the O3 (and HO2, RO2, etc) concentrations would vary significantly across these sites?

The four sites represented different NO_x level and we can see the impact of NOx level to the NO-NO_2 isotopic fractionations was significant.

O_3 (and HO_2, RO_2) concentrations impact the NO-NO_2 fractionation by altering the A values, which was reflected in the f(NO) parameter and the A value in our equations. From Eq. 7 and 8 we can know that we do not need to use O_3 (or HO_2, RO_2) concentration to calculate the isotopic fractionations as long as we know NO and NO_2 concentrations and the j(NO_2) values.

What are we really learning from site A vs B? They are both roadside. Given that there is such limited data to compare the model with, could the authors compare their roadside model to d15N(NO2) data collected by a roadside such as Felix and Elliott, 2014, "Isotopic composition of passively collected nitrogen dioxide emissions: Vehicle, soil, and livestock source signatures", Atmospheric Environment, 92, 359-366?

A and B are both roadside sites, however they have different NO_x concentrations. The NO_x concentrations at Anaheim site averaged at 58 ppb but the Evansville site only had 15 ppb. As a result, the isotopic fractionations at Anaheim was mainly controlled by EIE which showed high $\delta(NO_2)$-$\delta(NO_x)$ values (>10‰ throughout the day), but at Evansville, LCIE was more significant, thus the $\delta(NO_2)$- $\delta(NO_x)$ values can be as low as ~2‰ at noon.

Our discussion was less focused on the $\delta^{15}N$ values of NO_x sources but more focused on the impact of the NO_x level and photochemistry to the isotopic fractionations between NO and NO_2. Felix and Elliott, 2014 provided a good insight on the $\delta^{15}N(NO_2)$ values at roadside, and the NOx level at Felix and Elliott, 2014 study was similar to that of Anaheim. Therefore, we suggest at these sites, EIE will also be a dominate factor. Furthermore, in Felix and Elliott, 2014, there are little constrain on the differences between the $\delta^{15}N$ values of NO_2 and total NO_x, thus we are not able to further compare our work to theirs.

Also why not directly compare with what the model would predict quantitatively against the Walters 2018 work? And also predict the values for the Freyer work and compare?

Both Walters et al. 2018 and Freyer 1993 work used the same equation to calculate the isotopic shift which is similar to our approach. The only difference between their equation and our equation is that they assumed $\alpha 2$-$\alpha 1$=0 instead of the -10‰ measured in our experiment. We can see in these two works, the calculated isotopic shift values are similar to our results, suggesting the differences in LCIE may only slightly impact our results by a couple per mil in these conditions.

Lines 325-327: This conclusion is a bit strange. There is very little local HNO3 at Summit, Greenland. So drawing the conclusion based upon snow work (not atmosphere and snow) and assuming a direct link temporally between d15NO2 and d15NO3- seems a stretch. It might be more useful to look at Jarvis et al. (2009) instead – Jarvis, J. C., M. G. Hastings, E. J. Steig, and S. A. Kunasek (2009), Isotopic ratios in gas- phase HNO3 and snow nitrate at Summit, Greenland, J. Geophys. Res., 114, D17301, doi:10.1029/2009JD012134.

This is very good point. I have removed this part because directly using our model to interpret these data is not solid enough.

Line 329: what kinds of data and future environmental measurements should be conducted to validate this model? Help the community make this a reality!

We added a paragraph in the end of this section to address our limitations and future work. We suggest that future experiments, field observations and theoretical studies should be done to 1) verify our experimental results, 2) investigate the isotopic fractionation factor of reactions that converts NO_x into NO_y and nitrate, 3) study the isotopic effects of reactive nitrogen chemistry in the stratosphere amd 4) study the temperature dependence of these fractionation factors.

Supplement – This needs to be re-read and edited – there are a lot of typos. Some comments on the methods in the supplement – I have a number of questions: -what was the flow rate used to calculate the NO2 residence time ("reside" should be residence in the text)? -include more details of the denuder method – what company are these from? What were they coated with? How do you know they are quantitative in collection? Please show the collection efficiency data. And report how many times this was tested. -need to make it clearer where the 1.0268 value comes from – why is this value assumed here? Based upon the "best fit"? which really isn't a best fit (see comments from above). So what happens here if you do not assume a forced zero intercept? -make sure the editor's suggested technical corrections carry through the supplement as well.

We have gone through the supplementary material and fixed some typos. To answer the questions: we provided more detailed descriptions (e.g., flow rate, information about the denuder method) both in the main text and in the supplementary material. In the meantime, we have shown that our collection efficiency was nearly 100% by stating that we measured the NO_2 level on the exit of the denuder tubes when using the denuder tubes to collect NO_2 at 66 ppb, and the measured NO2 level at the denuder exit was below detection limit. We only conducted this control experiment once, but the testing lasts for over an hour, and the collection efficiency remained at 100% throughout this experiment. We also changed the 1.0268 to 1.0275 to align with the main text, and the reasons we used a zero intercept have been stated above.

Response to SC1

Dear Dr. Savarino,

Thank you for your comment! This is an excellent suggestion that will improve our paper.

We have removed the discussion that used our model to explain the Arctic snow nitrate isotopes. Instead, we pointed out some uncertainties that still exist in this field, and we suggest that future work is needed to further address these issues.

List of all the changes made in the manuscript:

1. We rewrite the abstract to provide more information toward a more general audience;

2. In the introduction part, we added some description about snow nitrate photolysis & redeposition, and introduced previous theoretical studies by Walters & Michalski, 2016 that calculated the KIE of NO+O3.

3. In the method section, we added detailed description of the chamber and our experiments, including the light source used, instruments that measured NO_x and O_3 concentrations, and control experiments testing 1) NO_2 wall loss, 2) $\delta^{15}N$ value of NO tank, 3) collection efficiency of denuder tubes and 4) blank. Additionally, we added the description of denuder tube coating procedure.

4. We limited our discussion to tropospheric chemistry because we realize our experiments can only represent the chemistry in the troposphere;

5. We also discussed the temperature effect of EIE and LCIE, which cannot be addressed by our experiments. We suggest future studies are needed to investigate these issues.

6. We added theoretical calculations that compared our measured LCIE results to the theoretical prediction using a ZPE shift model. These calculations showed good agreement with our measured values.

7. We also used the ZPE shift model to investigate the effect of light to the PHIFE, which was suggested to be minor (<0.5‰ shift when solar zenith angle vary from 0 to 85 degree).

8. We revised some symbols: j, k, f to be italic, and used $\Delta(NO_2\text{-}NO_x)$ and $\Delta(NO_2\text{-}NO)$ to represent $\delta(NO_2)\text{-}\delta(NO_x)$, $\delta(NO_2)\text{-}\delta(NO)$.

9. We clearly stated our assumptions before applying our model into the ambient environment (implication section).

10. We discussed the limitations of our study and suggested some future works to keep investigating this topic.

11. We revised the figures to match our changes in the manuscript; in the meantime, we added a sketch as Fig. 1C to illustrate our main point of this study.

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 poorly 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 to the combined isotopic fractionation (equilibrium isotopic exchange and photochemical cycle) between NO and NO_2 were 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 isotope exchange is 1.0275±0.0012, 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 ambient environment, although future work is needed to assess the isotopic fractionation factors of NO + $RO_2/HO_2 \rightarrow NO_2$. 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 dominate 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.

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1. Introduction

The nitrogen isotopic composition ($\delta^{15}N$) 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 $\delta^{15}N$ value of atmospheric nitrate (HNO_3, nitrate aerosols and nitrate ions in the precipitation and snow) imprints the $\delta^{15}N$ value of NO_x sources (Elliott et al., 2009; Kendall et al., 2007) thus many studies have used the $\delta^{15}N$ values of atmospheric 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 that may occur during photochemical cycling of NO_x could alter the $\delta^{15}N$ values as it partitions into NO_y (NO_y = atmospheric nitrate, NO_3, N_2O_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). Similarily, other complex reactive nitrogen chemistry, such as nitrate photolysis and re-deposition in ice and snow (Frey et al., 2009), may impact the $\delta^{15}N$ of NO_y and atmospheric nitrate. The fractionation between NO and NO_2 via isotope exchange has been suggested to be the dominant factor in determining the $\delta^{15}N$ of NO_2 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, NO_x and NO_y reactions, while most of these are still unknown, or, if calculated (Walters and Michalski, 2015), unverified by experiment. Since the atmospheric chemistry of NO_y varies significantly in different environments (e.g., polluted vs. pristine, night vs. day), the isotopic fractionations associated with NO_y chemistry are also likely to vary in different environments. These unknowns could potentially bias conclusions about NO_x source apportionment reached when using nitrogen isotopes. Therefore, understanding the isotopic

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fractionations between NO and NO$_2$ during photochemical cycling could improve our understanding of the relative role of source versus chemistry for controlling the δ^{15}N variations of atmospheric NO$_2$ and nitrate.

In general, there are three types of isotope fractionation effects associated with NO$_x$ chemistry. 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 NO$_x$ system is the ^{15}NO + ^{14}NO$_2$ ↔ ^{14}NO + ^{15}NO$_2$ 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 & Wolfsberg, 1957). In the NO$_x$ system this KIE would be manifest in the oxidation of NO into NO$_2$ by O$_3$/HO$_2$/RO$_2$. The third type is the photochemical isotope fractionation effect (PHIFE, Miller & Yung, 2000), which for NO$_x$ is the isotopic fractionation associated with NO$_2$ photolysis. All three fractionations could impact the δ^{15}N value of NO$_2$, and consequently atmospheric nitrate, but the relative importance of each may vary.

The limited number of studies on the EIE in the NO$_x$ cycle have significant uncertainties. Discrepancies in the EIE for ^{15}NO + ^{14}NO$_2$ ↔ ^{14}NO + ^{15}NO$_2$ have been noted in several studies. Theoretical calculations predicted isotope fractionation factors (α) ranging from 1.035 to 1.042 at room temperature (Begun & Fletcher, 1960; Monse et al., 1969; Walters & Michalski, 2015) due to the different apporximations used to calculate harmonic frequencies in each study. Likewise, two separate experiments measured different room temperature fractionation factors of 1.028±0.002 (Begun & 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 NO$_x$ concentrations (hundreds of µmol mol^{-1}), significantly higher than typical ambient atmospheric NO$_x$ levels

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(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, notable N_2O_4 and N_2O_3 at these high NO_x concentrations.

Even less research has examined the KIE and PHIFE occurring during NO_x cycling. The KIE of NO + O_3 has been theoretically calculated (Walters and Michalski, 2016) but has not been experimentally verified. The NO_2 PHIFE has not been experimentally determined or theoretically calculated. As a result, field observation studies often overlook the effects of PHIFE and KIE. Freyer et al. (1993) measured NO_x concentrations and the $\delta^{15}N$ values of NO_2 over a 1-year period at Julich, Germany and inferred a combined NO_x isotope fractionation factor (EIE+KIE+PHIFE) of 1.018±0.001. Freyer et al. (1993) suggested that the NO_x photochemical cycle (KIE and PHIFE) tends to diminish the equilibrium isotopic fractionation (EIE) between NO and NO_2. Even if this approach were valid, applying this single fractionation factor elsewhere, where NO_x, O_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_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_2 at photochemical equilibrium. First, we measured the N isotope fractionations between NO and NO_2 in an atmospheric simulation chamber at atmospherically relevant NO_x levels. Then, we provide mathematical solutions to assess the impact of NO_x level and NO_2 photolysis rate ($j(NO_2)$) 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. Lastly, using

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the calculated fractionation factors and the equations, we modeled the NO-NO$_2$ isotopic fractionations at several sites to illustrate the behavior of δ^{15}N values of NO$_x$ in the ambient environment.

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2. Methods

The experiments were conducted using a 10 m^3 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 O$_3$ into the chamber. NO was injected at 1 L min^{-1} from an in-house NO/N$_2$ cylinder (133.16 µmol mol^{-1} NO in ultra-pure N$_2$), and O$_3$ was generated by flowing 5 L min^{-1} zero-air through a flow tube equipped with a UV Pen-Ray lamp (UVP LLC., CA) into the chamber. NO and NO$_2$ concentrations were monitored in real time by chemiluminescence with a detection limit of 0.5 ppb (model CLD 88Y, Eco Physics, MI) as were O$_3$ concentrations using an UV absorption spectroscopy with a detection limit of 0.5 ppb (model 49, Thermo Scientific, CO). In each experiment, the actual amounts of NO and O$_3$ injected were calculated using measured NO$_x$ and O$_3$ concentrations after steady state was reached (usually within 1 h). The wall loss rate of NO$_2$ was tested by monitoring O$_3$ (29 nmol mol^{-1}) and NO$_x$ (62 nmol mol^{-1}) over a 4-hour period. After the NO and NO$_2$ concentrations reached steady state, no decrease in NO$_2$ concentrations was observed showing that chamber wall loss was negligible.

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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$_3$ ([O$_3$]<[NO]) was injected into the chamber to produce NO-NO$_2$ mixtures with [NO]/[NO$_2$] ratios ranged from 0.43 to 1.17. The N isotopes of these mixtures were used to

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investigate the EIE between NO and NO_2. The second set of experiments was conducted under irradiation of UV lights (300-500 nm, see supplementary material for irradiation spectrum). Under such conditions, NO, NO_2 and O_3 reached photochemical steady state, which combined the isotopic effects of EIE, KIE and PHIFE. In addition, three experiments were conducted to measure the $\delta^{15}N$ value of the tank NO. In each of these experiments, a certain amount of O_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_x was in the form of NO_2 with little O_3 (<3 nmol mol^{-1}) remaining in the chamber, such that the O_3+NO_2 reaction was negligible. The NO_2 in the chamber was then collected and its $\delta^{15}N$ value measured, which equates to the $\delta^{15}N$ value of the tank NO.

In all experiments, the concentrations of NO, NO_2 and O_3 were allowed to reach steady state, and the product NO_2 was collected from the chamber using a honeycomb denuder tube. The glass denuder tubes (Chemcomb 3500, Thermo Fisher Scientific) were coated with a solution of 10% KOH and 25% guaiacol in methanol and then dried by flowing N_2 gas through the denuder tube for 15 seconds (Williams and Grosjean, 1990, Walters et al., 2016). The NO_2 reacts with guaiacol coating and is converted into NO_2^- that is retained on the denuder tube wall (Williams and Grosjean, 1990). NO is inert to the denuder tube coating: a control experiment sampled pure NO using the denuder tubes, which did not show any measurable NO_2^-. The NO_2 collection efficiency of a single honeycomb denuder tube was tested in another control experiment: air containing 66 nmol mol^{-1} of NO_2 was drawn out of the chamber through a denuder tube, and the NO_2 concentration at the exit of the tube holder was measured and found to be below the detection limit (<1 nmol mol^{-1}), suggesting 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 and NO_2^- in the second denuder was below the detection limit indicating trivial break NO_2 breakthrough. The

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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 Purdue Stable Isotope Laboratory. For each sample, approximately 50 nmol of the NO_2^- extract 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_2^- to $N_2O_{(g)}$ (Casciotti & McIlvin, 2007; McIlvin & Altabet, 2005). The product N_2O was directed into a Thermo GasBench equipped with cryo-trap, then the $\delta^{15}N$ of the N_2O was measured using a Delta-V Isotope Ratios Mass Spectrometer. Six coated denuders 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 the blank from both sampling process and the chemical conversion process was negligible. The overall analytical uncertainty for $\delta^{15}N$ analysis was ±0.5 ‰ (1σ) based on replicate analysis of in house NO_2^- standards.

3. Results and Discussions

3.1. Equilibrium Isotopic Fractionation between NO and NO₂

The equilibrium isotope fractionation factor, $\alpha(NO_2\text{-}NO)$, is the ^{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:

$^{15}NO_2 + ^{14}NO \rightarrow ^{15}NO + ^{14}NO_2$ R1, rate constant = k_1

$^{15}NO + ^{14}NO_2 \rightarrow ^{15}NO_2 + ^{14}NO$ R2, rate constant = $k_2 = k_1 \times \alpha(NO_2\text{-}NO)$

where k_1 is the rate constant of the isotopic exchange, which was previously determined to be 8.14×10^{-14} $cm^3\ s^{-1}$ (Sharma et al., 1970). The reaction time required for NO-NO₂ 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

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The isotope equilibrium fractionation factor is then calculated to be:

$$\alpha(NO_2-NO)=\frac{[^{15}NO_2]\times[^{14}NO]}{[^{14}NO_2]\times[^{15}NO]}=\frac{R(NO_2)}{R(NO)} \qquad \text{Eq. (1)}$$

where $R(NO, NO_2)$ are the $^{15}N/^{14}N$ ratios of NO and NO_2. By definition, the $\delta^{15}N(NO)=(R(NO)/R(reference)-1)\times1000$‰ and $\delta^{15}N(NO_2)=(R(NO_2)/R(reference)-1)\times1000$ ‰, but hereafter, the $\delta^{15}N$ values of NO, NO_2 and NO_x will be referred as $\delta(NO)$, $\delta(NO_2)$ and $\delta(NO_x)$, respectively. Eq. (1) leads to:

$$\delta(NO_2)-\delta(NO)=(\alpha(NO_2-NO)-1)\times1000\text{‰}\times(1+\delta(NO))$$

$$=\varepsilon(NO_2-NO)\times(1+\delta(NO)) \qquad \text{Eq. (2)}$$

where $\varepsilon(NO_2\text{-}NO)$ is the isotope enrichment factor $\varepsilon(NO_2\text{-}NO)=(\alpha(NO_2\text{-}NO)-1)\times1000$‰, (Hoefs, 2009). Using Eq. (2) and applying NO_x isotopic mass balance ($\delta(NO_x)=f(NO_2)\times\delta(NO_2)+(1-f(NO_2))\times\delta(NO)$, $f(NO_2)=[NO_2]/([NO]+[NO_2])$) yields:

$$\delta(NO_2)-\delta(NO_x)=\varepsilon(NO_2-NO)\times(1+\varepsilon(NO_2-NO))\times(1+\delta(NO_2))\times(1-f(NO_2)) \qquad \text{Eq. (3)}$$

Here, $\delta(NO_x)$ equals to the $\delta^{15}N$ value of the cylinder NO and $f(NO_2)$ is the molar fraction of NO_2 with respect to total NO_x. Three experiments (see descriptions in method section) that measured $\delta(NO_x)$ showed consistent $\delta(NO_x)$ values of -58.7±0.8 ‰ (n = 3), indicating $\delta(NO_x)$ remained unchanged throughout the experiments (as expected for isotope mass balance). Thus, the $\delta(NO_x)$ can be treated as a constant in Eq. (3), and the slope of a linear regression of $(\delta(NO_2)-\delta(NO_x))/(1+\delta(NO_2))$ versus $1-f(NO_2)$ yields $\varepsilon(NO_2\text{-}NO)/(1+\varepsilon(NO_2\text{-}NO))$.

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The plot of $(\delta(NO_2)-\delta(NO_x))/(1+\delta(NO_2))$ as a function of $1-f(NO_2)$ values from five experiments yielded an $\varepsilon(NO_2\text{-}NO)$ value of 27.5±1.2 ‰ at room temperature. This fractionation factor is comparable to previously measured values but with some differences. Our result agrees well with the $\alpha(NO_2\text{-}NO)$ value of 1.028±0.002 obtained by Begun and Melton (1956) at room temperature. However, Walters et al., (2016) determined the $\alpha(NO_2\text{-}NO)$ values of NO-NO_2 exchange in a 1-liter reaction vessel, which showed a slightly higher $\alpha(NO_2\text{-}NO)$ 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) that 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_2O_4 by over an order of magnitude (Barney & Finlayson-Pitts, 2000; Saliba et al., 2001), which at isotopic equilibrium is enriched in ^{15}N compared to NO and NO_2 (Walters & Michalski, 2015). Therefore, their measured $\alpha(NO_2\text{-}NO)$ might be slightly higher than the actual $\alpha(NO_2\text{-}NO)$ value. In this work, the 10 m^3 chamber has a much smaller surface to volume ratio relative to Walters et al. (2016) which minimizes wall effects, and the walls were made of Teflon that minimize NO_2 surface reactivity, which was evidenced by the NO_2 wall loss control experiment. Furthermore, the low NO_x mixing ratios in our experiments minimized N_2O_4 and N_2O_3 formation. At NO and NO_2 concentrations of 50 nmol mol^{-1} the steady state concentrations of N_2O_4 and N_2O_3 were calculated to be 0.014 and 0.001 pmol mol^{-1}, respectively (Atkinson et al., 2004). Therefore, we suggest our measured $\alpha(NO_2\text{-}NO)$ value (1.0275±0.0012) may better reflect the room temperature (298 K) NO-NO_2 EIE in the ambient environment.

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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 α(NO_2-NO) follows a similar temperature dependence pattern calculated in Walters et al. (2016). Walters et al. (2016) suggested that, the ε(NO_2-NO) value would be 4.7 ‰ higher at 273 K and 2.0 ‰ lower at 310 K, relative to room temperature (298 K). Using this pattern and our experimentally determined data, we suggest the α(NO_2-NO) values at 273 K, 298 K and 310 K are 32.2±1.2 ‰, 27.5±1.2 ‰ and 25.5±1.2 ‰, respectively. This 6.7‰ variation at least partially contribute to the daily and seasonal variations of $\delta^{15}N$ values of NO_2 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 NO_x will compete with the isotope exchange fractionations between NO and NO_2. The NO-NO_2 photochemical cycle in the chamber was controlled by the Leighton cycle: NO_2 photolysis and the NO + O_3 reaction. This is because there were no VOCs in the chamber so no RO_2 was produced, which excludes the NO + RO_2 reaction. Likewise, the low water vapor content (RH<10%) and the minor flux of photons < 310 nm results in minimal OH production and hence little HO_2 formation and subsequently trivial amount of NO_2 would be formed by NO + HO_2. Applying these limiting assumptions, the EIE between NO and NO_2 (R1-R2) were only competing with the KIE (R3-R4) and the PHIFE in R5-R6:

$^{14}NO_2 \rightarrow {}^{14}NO+O$ R3, rate constant=*j*(NO_2)

$^{15}NO_2 \rightarrow {}^{15}NO+O$ R4, rate constant=*j*(NO_2)×α_1

$^{14}NO+O_3 \rightarrow {}^{14}NO_2+O_2$ R5, rate constant=k_5

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$^{15}NO+O_3 \rightarrow ^{15}NO_2+O_2$ R6, rate constant=$k_5 \times \alpha_2$

In which $j(NO_2)$ is the NO_2 photolysis rate (1.4×10^{-3} s^{-1} in these experiments), k_5 is the rate constant for the $NO+O_3$ reaction (1.73×10^{-14} cm^3 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 (R1-R2), KIE and PHIFE (R3-R6), but none of them quantified the relative importance of the two processes, nor were α_1 or α_2 values experimentally determined. Here we provide the mathematical solution of EIE, KIE and PHIFE to illustrate how R1-R6 affect the isotopic fractionations between NO and NO_2.

First, the NO_2 lifetime with respect to isotopic exchange with NO ($\tau_{exchange}$) and photolysis (τ_{photo}) was determined:

$$\tau_{exchange} = \frac{1}{k_1 \times [NO]} \qquad \text{Eq. (4)}$$

$$\tau_{photo} = \frac{1}{j(NO_2)} \qquad \text{Eq. (5)}$$

We then define an A factor:

$$A = \begin{cases} \frac{\tau_{exchange}}{\tau_{photo}} & \text{when } j(NO_2) \neq 0 \\ 0 & \text{when } j(NO_2) = 0 \end{cases} \qquad \text{Eq. (6)}$$

Using R1-R6 and Eq. (1)-(6), we solved steady-state $\delta(NO_2)$ and $\delta(NO)$ values (see calculations in supplementary material). Our calculations show that the $\delta(NO_2)$-$\delta(NO)$ and $\delta(NO_2)$-$\delta(NO_x)$ values at steady state can be expressed as functions of α_1, α_2, $\alpha(NO_2\text{-}NO)$ and A:

$$\delta(NO_2) - \delta(NO)\ (‰) = \frac{(\alpha_2-\alpha_1) \times A + (\alpha(NO_2-NO)-1)}{A+1} \times 1000\ ‰ \qquad \text{Eq. (7)}$$

$$\delta(NO_2) - \delta(NO_x)\ (‰) = \frac{(\alpha_2-\alpha_1) \times A + (\alpha(NO_2-NO)-1)}{A+1} \times (1 - f(NO_2)) \times 1000\ ‰ \qquad \text{Eq. (8)}$$

Equation (7) shows the isotopic fractionation between NO and NO_2 ($\delta(NO_2)$-$\delta(NO)$) is largely determined by A, the EIE factor ($\alpha(NO_2\text{-}NO)$-1) and the (α_2-α_1) factor. This (α_2-α_1) represents a

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$$A = \begin{cases} \frac{\tau_{exchange}}{\tau_{photo}} & when\ j_{NO_2} \neq 0 \\ 0 & when\ j_{NO_2} = 0 \end{cases} \rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow \text{Eq. (4)¶}$$

in which $\tau_{exchange}$ is

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combination of KIE and PHIFE, suggesting they act together as one factor; therefore, we name the (α_2-α_1) factor Leighton Cycle Isotopic Effect, i.e., LCIE. Using measured δ(NO$_2$)-δ(NO) values, A values, and the previously determined EIE factor, we calculated that the best fit for the LCIE factor was -10±5 ‰ (r = 0.52, Fig. 1B). The uncertainties in the LCIE factor are 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 (1.4×10^{-3} s^{-1}) under the chamber irradiation conditions.

This LCIE factor determined in our experiments is in good agreement with theoretical calculations. Walters and Michalski (2016) previously used an *ab initio* approach to determine an α_2 value of 0.9933 at room temperature, 0.9943 at 237 K and 0.9929 at 310 K. The variation of α_2 values from 273 K to 310 K is only ±0.7 ‰, significantly smaller than our experimental uncertainty. The α_1 value was calculated using a ZPE shift model (Miller & Yung, 2000) to calculate the isotopic fractionation of NO$_2$ 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}NO$_2$ and ^{14}NO$_2$ absorption cross-section as a function of wavelength, thus α_1 values do not vary by temperature. The ^{15}NO$_2$ absorption cross-section was calculated by shifting the ^{14}NO$_2$ absorption cross-section by the ^{15}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 α_1 value was 1.0023. Therefore, the theoretically predicted α_2-α_1 value should be -0.0090, i.e., -9.0±0.7 ‰ when temperature ranges from 273 K to 310 K. This result shows excellent agreement with our experimentally determined room temperature α_2-α_1 value of -10±5 ‰.

This model was then used to evaluate the variations of α_1 value to different lighting conditions. The TUV model (TUV5.3.2, Madronich & Flocke, 1999) was used to calculate the

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solar wavelength spectrum at three different conditions: early morning/late afternoon (solar zenith angle=85 degree), mid-morning/afternoon (solar zenith angle=45 degree), noon (solar zenith angle=0 degree). These spectrums were used in the ZPE shift model to calculate the α_1 values, which are 1.0025, 1.0028, and 1.0029 at solar zenith angles of 85, 45 and 0 degree, respectively. These values, along with the predicted α_1 value in the chamber, showed a total span of 0.6‰ (1.0026 ±0.0003), which is again significantly smaller than our measured uncertainty. Therefore, we suggest that our experimentally determined LCIE factor (-10±5 ‰) can be used in most tropospheric solar irradiation spectrums.

The equations can also be applied in tropospheric environments to calculate the combined isotopic fractionations of EIE and LCIE for NO and NO_2. First, the NO_2 sink reactions (mainly NO_2+OH in the daytime) are at least 2-3 orders of magnitude slower than the Leighton cycle and the NO-NO_2 isotope exchange reactions (Walters et al., 2016), therefore their effects on the $\delta(NO_2)$ should be minor. Second, although the conversion of NO into NO_2 in the ambient environment is also controlled by NO + RO_2 and HO_2 in addition to $NO+O_3$ (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 $\delta(NO_2)-\delta(NO)$ 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 $5.0\pm1.0\times10^{-3}$, 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. This agreement suggests the $NO+RO_2/HO_2$ reactions might have similar fractionation factors as $NO+O_3$. Therefore, we suggest

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Eq. (7) and (8) can be used to estimate the isotopic fractionations between NO and NO_2 in the troposphere (Fig. 1C).

3.3 Calculating nitrogen isotopic fractionations of NO-NO_2

First, Eq. (7) was used to calculate the $\Delta(NO_2\text{-}NO) = \delta(NO_2)-\delta(NO)$ at a wide range of NO_x concentrations, $f(NO_2)$ and $j(NO_2)$ values (Fig. 2A-D). $j(NO_2)$ values of 0 s^{-1} (Fig. 2A), 1.4×10^{-3} s^{-1} (Fig. 2B), 5×10^{-3} s^{-1} (Fig. 2C) and 1×10^{-2} s^{-1} (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 $j(NO_2)$ value, and the $\Delta(NO_2\text{-}NO)$ values were calculated as a function of the A value, which was derived from NO_x concentration and $f(NO_2)$. The A values have a large span, from 0 to 500, depending on the $j(NO_2)$ value and the NO concentration. When A=0 ($j(NO_2)=0$) and $f(NO_2)<1$ (meaning NO-NO_2 coexist and $[O_3]=0$), Eq. (7) and (8) become Eq. (2) and (3), showing the EIE was the sole factor, the $\Delta(NO_2\text{-}NO)$ values were solely controlled by EIE which has a constant value of +27.5 ‰ at 298K (Fig. 2A). When $j(NO_2)>0$, the calculated $\Delta(NO_2\text{-}NO)$ values showed a wide range from -10.0 ‰ (controlled by LCIE factor: $\alpha_2-\alpha_1=-10$ ‰) to +27.5 ‰ (controlled by EIE factor: $\alpha(NO_2\text{-}NO)-1 = +27.5$ ‰). Fig. 2B-D display the transition from a LCIE-dominated regime to an EIE-dominated regime. The LCIE-dominated regime is characterized by low $[NO_x]$ (<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: $\Delta(NO_2\text{-}NO) = (\alpha_2-\alpha_1)\times1000$ ‰, suggesting the LCIE almost exclusively controls the NO-NO_2 isotopic fractionation. The $\Delta(NO_2\text{-}NO)$ 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 $[NO_x]$ (>20 nmol

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mol^{-1}) and low $f(NO_2)$ (< 0.6), representative of regions with intensive NO emissions, e.g., near roadside or stack plumes (Clapp & Jenkin, 2001; Kimbrough et al., 2017). In this case, the $\tau_{exchange}$ are relatively short (10-50 s) compared to the τ_{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 $\Delta(NO_2\text{-}NO)$ values (>20 ‰). Between the two regimes, both EIE and LCIE are competitive and therefore it is necessary to use Eq. (7) to quantify the $\Delta(NO_2\text{-}NO)$ values.

Fig. 2 also implies that changes in the $j(NO_2)$ value can cause the diurnal variations in $\Delta(NO_2\text{-}NO)$ values. Changing $j(NO_2)$ would affect the value of A and consequently the NO-NO_2 isotopic fractionations in two ways: 1) changes in $j(NO_2)$ value would change the photolysis intensity, therefore the τ_{photo} value; 2) in addition, changes in $j(NO_2)$ value would also alter the steady state NO concentration, therefore changing the $\tau_{exchange}$ (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 atmospheric chemistry models.

We then calculated the differences of $\delta^{15}N$ values between NO_2 and total NO_x, e.g. $\Delta(NO_2\text{-}NO_x) = \delta(NO_2)\text{-}\delta(NO_x)$ in Fig. 2E-H. Since $\Delta(NO_2\text{-}NO_x)$ are connected through the observed $\delta^{15}N$ of NO_2 (or nitrate) to the $\delta^{15}N$ of NO_x sources, this term might be useful in field studies (e.g., Chang et al., 2018; Zong et al., 2017). The calculated $\Delta(NO_2\text{-}NO_x)$ values (Fig. 2E-H) also showed a LCIE-dominated regime at low [NO_x] and an EIE-dominated regime at high [NO_x]. The $\Delta(NO_2\text{-}NO_x)$ values were dampened by the 1-$f(NO_2)$ factor comparing to $\Delta(NO_2\text{-}NO)$, as shown in Eq. (3) and (8): $\Delta(NO_2\text{-}NO_x) = \Delta(NO_2\text{-}NO)\times(1\text{-}f(NO_2))$. At high $f(NO_2)$ values (>0.8), the differences between $\delta(NO_2)$ and $\delta(NO_x)$ were less than 5 ‰, thus the measured $\delta(NO_2)$ values were similar to $\delta(NO_x)$, although the isotopic fractionation between NO and NO_2 could be noteworthy. Some

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ambient environments with significant NO emissions or high NO_2 photolysis rates usually have $f(NO_2)$ values between 0.4-0.8 (Mazzeo et al., 2005; Vicars et al., 2013). In this scenario, the $\Delta(NO_2\text{-}NO_x)$ 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 $j(NO_2)=1.4\times10^{-3}$ s^{-1}, 5×10^{-3} s^{-1}, 1×10^{-2} s^{-1}, respectively. These significant differences again highlighted the importance of both LCIE and EIE (Eq. (7) and (8)) in calculating the $\Delta(NO_2\text{-}NO_x)$. In the following discussion, we assume 1) the α_1 value remain constant (see discussion above), 2) the $NO+RO_2/HO_2$ reactions have the same fractionation factors (α_2) as $NO+O_3$, and 3) both EIE and LCIE do not display significant temperature dependence, then use Equations (7) and (8) and this laboratory determined LCIE factor (-10 ‰) to calculate the nitrogen isotopic fractionation between NO and NO_2 at various tropospheric atmospheric conditions.

4. Implications

The daily variations of $\Delta(NO_2\text{-}NO_x)$ values at two roadside NO_x monitoring sites were predicted to demonstrate the effects of NO_x concentrations to the NO-NO_2 isotopic fractionations. Hourly NO and NO_2 concentrations were acquired from a roadside site at Anaheim, CA (https://www.arb.ca.gov) and an urban site at Evansville, IN (http://idem.tx.sutron.com) on July 25, 2018. The hourly $j(NO_2)$ values output from the TUV model (Madronich & Flocke, 1999) at these locations was used to calculate the daily variations of $\Delta(NO_2\text{-}NO_x)$ values (Fig. 3A, B) by applying Eq. (8). Hourly NO_x concentrations were 12-51 nmol mol^{-1} at Anaheim and 9-38 nmol mol^{-1} at Evansville and the $f(NO_2)$ 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 $\Delta(NO_2\text{-}NO_x)$ values using Eq. (8) showed significant diurnal variations. During the nighttime, the isotopic

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fractionations were solely controlled by the EIE, the predicted $\Delta(NO_2\text{-}NO_x)$ 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 $\Delta(NO_2\text{-}NO_x)$ values to +9.8±1.7 ‰ at Anaheim and +3.1±1.5 ‰ at Evansville while the $f(NO_2)$ values at both sites remained similar. The lowest $\Delta(NO_2\text{-}NO_x)$ values for both sites (+7.0 ‰ and +1.7 ‰) occurred around noon when the NO_x photolysis was the most intense. In contrast, if one neglects the LCIE factor in the daytime, the $\Delta(NO_2\text{-}NO_x)$ 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-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 $\Delta(NO_2\text{-}NO_x)$ values 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 $j(NO_2)$ 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 $\delta(NO_x)$ ($\Delta(NO_2\text{-}NO_x) = 0$). In the daytime a certain amount of NO was produced by direct NO emission and NO_2 photolysis but the $f(NO_2)$ was still high (0.73±0.08). Our calculation suggested the daytime $\Delta(NO_2\text{-}NO_x)$ values should be only +1.3±3.2 ‰ with a lowest value of -1.3 ‰. These $\Delta(NO_2\text{-}NO_x)$ values were similar to the observed and modeled summer daytime $\delta(NO_2)$ values in West Lafayette, IN (Walters et al., 2018), which suggest the average daytime $\Delta(NO_2\text{-}NO_x)$ values at NO_x = 3.9±1.2 nmol mol^{-1} should range from +0.1 ‰ to +2.4 ‰. In this regime, we suggest the $\Delta(NO_2\text{-}NO_x)$ values were generally small due to the significant contribution of LCIE and high $f(NO_2)$.

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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 $\Delta(NO_2\text{-}NO_x)$ 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_2 ratios. Here the isotopes of NO_x were almost exclusively controlled by the LCIE due to the high A values (>110). The $\Delta(NO_2\text{-}NO_x)$ 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 suggest that the isotopic fractionations between NO and NO_2 were almost completely controlled by LCIE at 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_2O_5+H_2O) are still unknown, more studies are needed to fully explain the daily and seasonal variations of $\delta(NO_3^-)$ at remote regions.

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_2O_5), KIE (formation of NO_3, N_2O_5 and nitrate) and PHIFE (photolysis of NO_3, N_2O_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 → HNO_3 reaction needs investigation. Such studies could help us modeling

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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. 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 troposphere and stratosphere, and the temperature dependence could also 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 ($j(NO_2)$) to the relative importance of EIE and LCIE. The EIE and LCIE isotope fractionation factors at room temperature, were determined to be 1.0275±0.0012 and 0.990±0.005, respectively. These calculations and measurements can be used to determine the steady state $\Delta(NO_2\text{-}NO)$ and $\Delta(NO_2\text{-}NO_x)$ values at room temperature. Subsequently we applied our equations to polluted, clean and remote sites to model the daily variations of $\Delta(NO_2\text{-}NO_x)$ values. We found that the $\Delta(NO_2\text{-}NO_x)$ 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 $\Delta(NO_2\text{-}NO_x)$ values. Our work provided a mathematical approach to quantify the nitrogen isotopic

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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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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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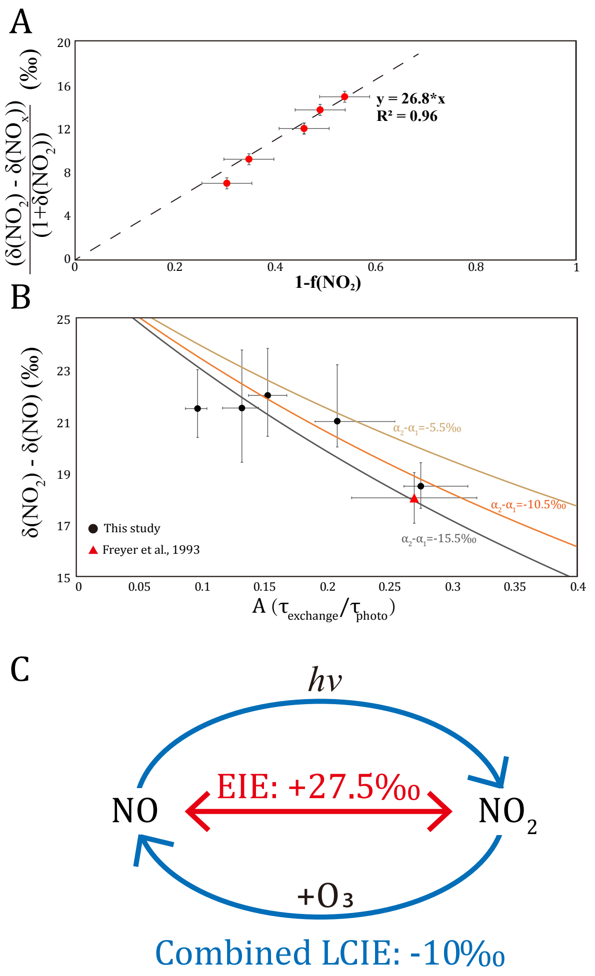
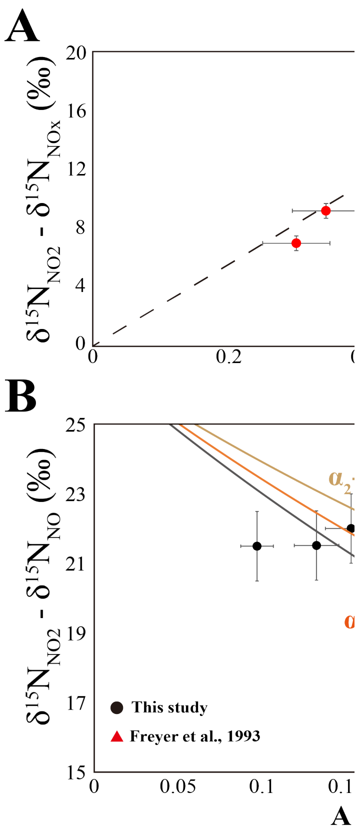


Fig. 1 $\delta^{15}N$ of NO_2 collected in dark and UV irradiation experiments. **A.** Results from five dark experiments yielded a line with $\varepsilon(NO_2\text{-}NO)/(1+\varepsilon(NO_2\text{-}NO))$ value of 26.8 ‰ and $\varepsilon(NO_2\text{-}NO)$ value of 27.5 ‰; **B.** Results from five UV irradiation experiments (black points) and a previous field study (red triangle). The three lines represent different $(\alpha_2\text{-}\alpha_1)$ values: the $(\alpha_2\text{-}\alpha_1)$=-10 ‰ line showed the best fit to our experimental data as well as the previous field observation; **C.** a sketch of the isotopic fractionation processes between NO and NO_2.



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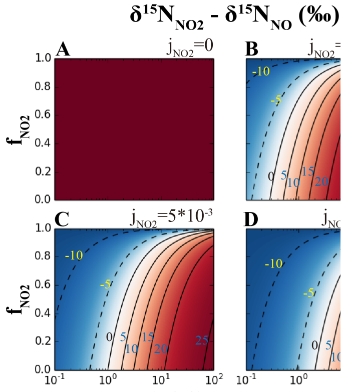

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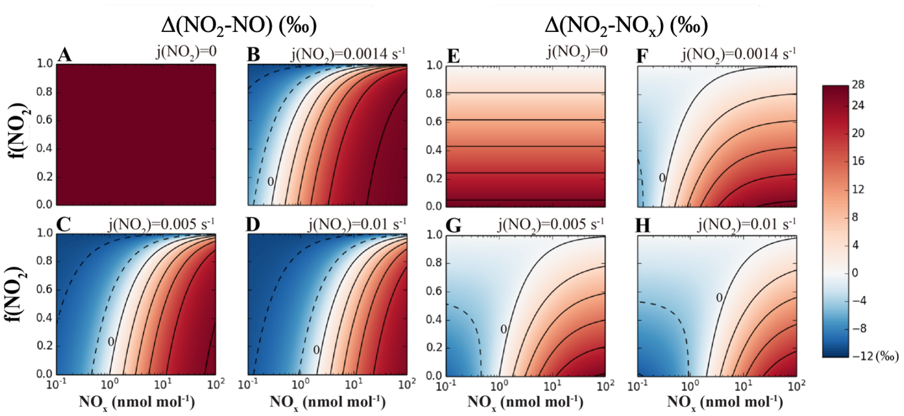

Fig. 2 Calculating isotopic fractionation values between NO-NO_2 (Δ(NO_2-NO), **A-D**) and NO_x-NO_2 (Δ(NO_2-NO_x), **E-H**) at various *j*(NO_2), NO_x level and *f*(NO_2) using Eq. (7) and (8). Each panel represents a fixed *j*(NO_2) value (showing on the upper right side of each panel), and the fractionation 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 on each panel except for A and E.

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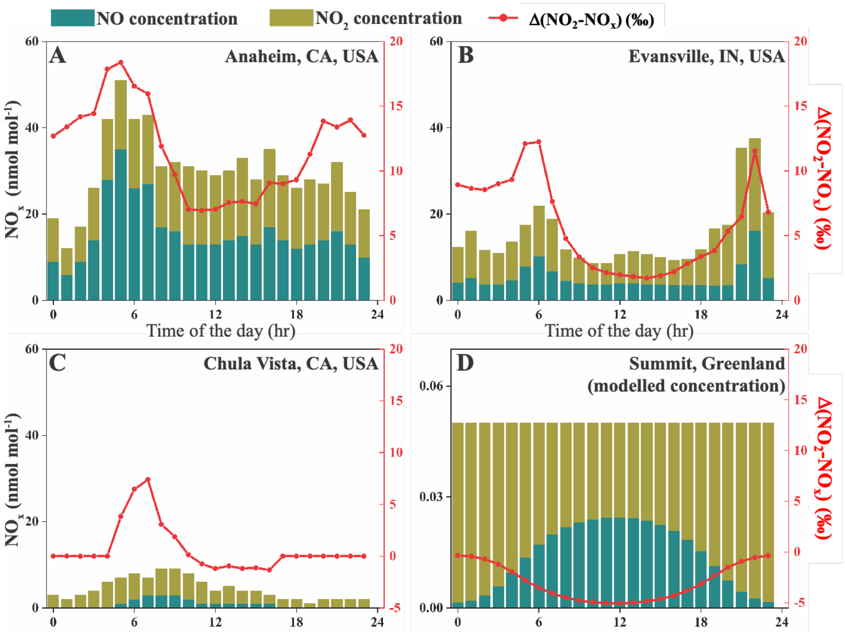
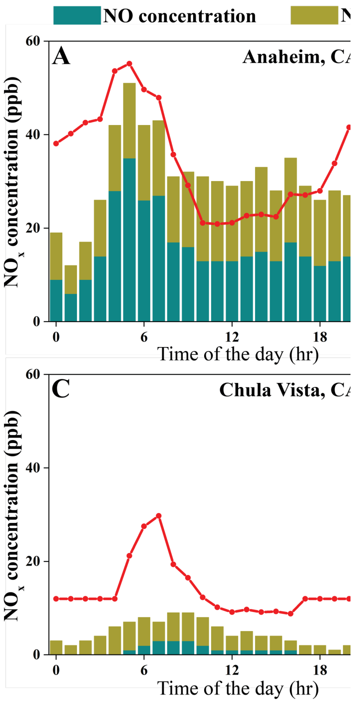


Fig. 3 NO$_x$ concentrations and calculated Δ(NO$_2$-NO$_x$) values at four sites. Stacked bars show the NO and NO$_2$ concentrations extracted from monitoring sites (A-C) or calculated using 0-D box model (D); the red lines are Δ(NO$_2$-NO$_x$) values at each site.



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