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Interactive comment on “Quantifying the nitrogen equilibrium and photochemistry-induced isotopic effects between NO and NO_2” *by* Jianghanyang Li et al.

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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. We also attached a PDF version of this response in case there is formatting issue.

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 ïĄď15N of NOx in the method section. In short, we measured the ïĄď15N of NOx in three different experiments. In each experiment, we inject same amount of NO and O3 to produce pure NO2, then we analyze the ïĄď15N value of the NO2. Because we can see that 100% of NOx in these experiments were in the form of NO2, therefore the measured ïĄď15N value can be used to represent the ïĄď15N of source NOx.

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 ïĄď18O first, then calculate the ïĄď17O value assuming mass dependent fractionation, then use these to correct for ïĄď15N signal. We notice that this method did not account for mass independent fractionation so it could shift the absolute ïĄď15N value (assuming O17 excess=30‰ by as much as 1.5‰Ḣowever, all the data shown on Figure 1A are ïĄď(NO2)-ïĄď(NOx), and both ïĄď(NO2) and ïĄď(NOx) have the same isobaric shift because they were measured using the same sampling & analysis method. So, when calculating the ïĄď(NO2)-ïĄď(NOx) 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 ïĄď15N values of source NOx (in these experiments f(NO)=0 and ïĄď(NO2)-ïĄď(NOx)=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 AâĹij0.1 and AâĹij0.15 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 Âż 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=$\sum(y\_i - f\_i)2inwhichyiistheobservedvalueandfiisthepredictedvaluebythefitline.Weattributethedev$

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 N2O4 and N2O3 were negligible. Also, we have mentioned that we conducted a control experiment to evaluate NO2 wall loss but did not observe any NO2 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 NO2 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, NO2 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 NO2, 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 ïĄď15N values but this should be cancelled out when we calculate the ïĄď(NO2)-ïĄď(NOx) 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 ïĄď15N(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 NO2 and measured the ïĄď15N values of NO2 to represent the ïĄď15N of NOx. All three experiments showed consistent ïĄď15N values, therefore we suggest the ïĄď15N value of NOx 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 ïĄď(NO2)-ïĄď(NO) values in each experiment, we calculated the error using the standard deviations of ïĄď(NO2)-ïĄď(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 N2O4 and N2O3 were negligible. Also, we have mentioned that we conducted a control experiment to evaluate NO2 wall loss but did not observe any NO2 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 ïĄď(NOx) is determined using the same method as ïĄď(NO2) 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 ïĄě=(α-1)*1000‰ we know ïĄě2-ïĄě1=(α2-α1)*1000‰Ṫo introduce as little symbols as possible, we did not use ïĄě 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 α1 value did not vary significantly with a changing j(NO2). Therefore, we will use this -10‰ in the following discussion assuming the α1 value remain constant, and 2) the NO+RO2/HO2 reactions have the same fractionation factors (α2) as NO+O3.

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 NO2 in dark condition (j(NO2)=0). In this scenario, EIE solely controls the isotopic fractionation therefore the ïĄď(NO2)-ïĄď(NO) should be a constant no matter how NOx 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 “NOx emission” to “total NOx”.

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 NOx level and we can see the impact of NOx level to the NO-NO2 isotopic fractionations was significant. O3 (and HO2, RO2) concentrations impact the NO-NO2 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 O3 (or HO2, RO2) concentration to calculate the isotopic fractionations as long as we know NO and NO2 concentrations and the j(NO2) 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 NOx concentrations. The NOx 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 ïĄď(NO2)-ïĄď(NOx) values (>10‰ throughout the day), but at Evansville, LCIE was more significant, thus the ïĄď(NO2)- ïĄď(NOx) values can be as low as ∼2‰ at noon. Our discussion was less focused on the ïĄď15N values of

NOx sources but more focused on the impact of the NOx level and photochemistry to the isotopic fractionations between NO and NO2. Felix and Elliott, 2014 provided a good insight on the ïĄď15N(NO2) 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 ïĄď15N values of NO2 and total NOx, 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 α2-α1=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 NOx into NOy 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 NO2 level on the exit of the denuder tubes when using the denuder tubes to collect NO2 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.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-1126/acp-2019-1126-AC3-supplement.pdf

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