Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-1126-RC2, 2020

Atmospheric Chemistry and Physics Discussions
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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.

Anonymous Referee #2

Received and published: 16 March 2020

This work presents a framework for interpreting isotope effects associated with NO and NO2 cycling in the atmosphere. The study utilizes controlled (chamber-based) experiments to quantify equilibrium and Leighton cycle based isotope effects, and then report under what conditions these effects could be important. The results are certainly important and warrant consideration for publication. Quantifying these effects is critical to being able to incorporate the isotopic composition of nitrogen oxides as a tracer in future models.

There are a number of important issues to address in the work. Here are general comments:

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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. Second, was the d15N data of all samples corrected for potential isobaric influences 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 changes 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 signal 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?

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

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to room temperature. So is it possible that the field determined value is showing a temperature dependence relative to the controlled experiments?

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?

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)?

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?

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.

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. Line 38: remove “the” before chemistry Lines 46-54: Please separate this into at least two separate sentences. Lines 61-63: What drives the difference in the theoretical predictions for this EIE? 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? 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. 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. Line 83: atmospheric should be "atmospherically" Line 88: change "NOx nitrogen isotopes" to something more correct like isotopic composition of NOx. 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! 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? 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? Line 129: difference should be "ratio of" correct? Line 140: I don't understand the formatting here with d(15N, 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? Lines 156: Where does the error on the 26.8 value come from? This is not represented in the figure. 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? 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? Lines 174-176: What exactly were the wavelengths of the blacklight used in the experiments? Lines 186-189: $\alpha 2$ value was determined in Walters and Michalski, 2016 ab initio study as referenced above. 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? 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! 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. Line 237: I do not see how this shown in Figure 2A. 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.

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?

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?

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?

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

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 more clear 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.

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