

## 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  $0.990 \pm 0.005$  at room temperature. However, this must be for a certain insolation spectrum and concentrations of O<sub>3</sub>, HO<sub>2</sub>, RO<sub>2</sub>? 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<sub>3</sub> solely controls the NO<sub>x</sub> 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<sub>2</sub>/HO<sub>2</sub> are similar to that of NO+O<sub>3</sub>.

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 O<sub>3</sub>, HO<sub>2</sub>, and RO<sub>2</sub>. 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<sub>3</sub>, HO<sub>2</sub>, and RO<sub>2</sub>. 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<sub>2</sub> and j(NO<sub>2</sub>) 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 NO<sub>2</sub> by O<sub>3</sub> in conditions with low concentrations of HO<sub>2</sub> and RO<sub>2</sub>, which will play a role in the atmosphere. They suggest that the HO<sub>2</sub> and RO<sub>2</sub> oxidations of NO might have a similar KIE as the O<sub>3</sub> 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<sub>3</sub> is similar to that of HO<sub>2</sub> and RO<sub>2</sub>, 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<sub>3</sub>, HO<sub>2</sub> or RO<sub>2</sub>, if we know both NO and NO<sub>2</sub> concentrations. The existence of O<sub>3</sub>, HO<sub>2</sub> or RO<sub>2</sub> would be reflected in the NO/NO<sub>2</sub> ratio at a given  $j(\text{NO}_2)$  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 NO<sub>x</sub> 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.