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Atmospheric Chemistry and Physics Discussions

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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Review of Quantifying the nitrogen equilibrium and photochemistry-induced isotopic effects between NO and NO_2 by Li, Zhang, Michalski, Orlando and Tyndall.

This paper is a professional investigation of an important question that yields valuable insight. Chamber experiments were carried out to measure the isotopic fractionation factors of the Equilibrium Isotopic Effect (EIE) and the Leighton Cycle Induced Isotope Effect (LCIE). A model was used to predict the variations that can be expected in field measurements based on the EIE and LCIE. The experiments seem to yield valuable results and my comments mainly concern model validation (limited because of lack

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Discussion paper

of data), and I am not convinced the LCIE result is perfectly general. I would like to see more discussion regarding how the LCIE will change with the widely variable conditions of the atmosphere including actinic flux spectrum, temperature, pressure, concentrations of O_3, RO_2 and HO_2, etc.

Experiment:
The experimental method and analysis seem sound. For example the use of the honeycomb denuder tube to trap NO_2 and reaction chamber with hydrophobic/inert teflon walls which will minimize interference from surface adsorbed water.

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.

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 O_3, HO_2, RO_2? Please include the conditions. How much will the LCIE change with the changes in conditions found in the atmopshere, or can we take this result to be applicable throughout the atmosphere?

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_3, HO_2, and RO_2. Please present a discussion of these factors.

What affect will the formation of PANs/addition of this equilibrim, have on the LCIE?

Please comment on the LCIE that would be observed in the stratosphere.

In the authors' experiment, NO is converted to NO_2 by O_3 in conditions with low con-

centrations of HO_2 and RO_2, which will play a role in the atmosphere. They suggest that the HO_2 and RO_2 oxidations of NO might have a similar KIE as the O_3 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.

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 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?

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.

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

I am not sure why the TLA (three letter acronymn) '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.

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

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

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

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?

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