

Interactive comment on “Isotope effects in N₂O photolysis from first principles” by J. A. Schmidt et al.

J. A. Schmidt et al.

johanalbrechtschmidt@gmail.com

Received and published: 4 August 2011

We are grateful for and very pleased with the valuable comments we received from Dr. Marcus and Dr. Griffith. We agree with the (minor) specific comments presented by the referees.

Dr. Marcus noted that it seems inappropriate to characterize the studies of the Marcus group (Prakash et al. 2005; Chen et al. 2008, 2010) as being “semi-empirical”. The arguments presented by Dr. Marcus have convinced us. In the revised manuscript we now refer to these studies as being “reflection principle based”. We believe that this is a more accurate common characteristic for the work presented by the Marcus group.

Dr. Griffith presented a list of minor technical comments and corrections. We tried to

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answer all comments and corrections:

P16077:

L15: changed “it’s” to “its”

L20: added the following sentences; “The model took into account that heavy isotopologues, i.e. ¹⁴N₂¹⁸O, have a smaller ground state vibrational energy and the overall absorptions band of these isotopologues therefore tend to be shifted to higher energies. The absorption cross section (and the rate of photolysis) is therefore smaller for the heavy isotopologues on the low-energy side of the cross section. Since N₂O is primarily photolysed on the low energy side this causes the remaining pool of N₂O to be enriched in heavy isotopes.”

P16078:

L10: Added citation to Kaiser and Röckmann (2005), to clarify which budget we are referring to. And changed “0.4%” to “0.5%”.

L18: Added the word “one” so it reads “... the only one to be based ...”

L27: added the following to end of sentence; “together with an ab initio excited state PES and a Transition Dipole Moment surface (TDM)” Note that we have defined the acronym “TDM” in the sentence above.

L27: Removed the word “And”

P16083:

Eq. 5: I have added two extra equations to make the derivation more transparent.

P16090

L8: Changed to “mass independent oxygen isotope anomaly”

Sect. 2.3.1 has been changed.

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Caption for Figure 6: This caption has been expanded.

Caption for Figure 7: Added "The fractionation constants of this study are calculated using Eqs. (1) and (4)."

Finally we have also:

Changed the abstract slightly.

Changed caption for Figure 5 slightly.

Changed color in Figure 4.

Completed citation for Schmidt et al. (2011)

Added citation to McLinden et al. (2002) and Schinke (2011).

And corrected a few typos.

We would like to again thank the referees for taking time to carefully review our manuscript and thereby help improve it.

Sincerely,

Johan Albrecht Schmidt, Matthew Stanley Johnson and Reinhard Schinke.

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