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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Isotope effects in N_2O photolysis from first principles" *by* J. A. Schmidt et al.

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In 1997 Yung and Miller postulated that zero point energy differences in different isotopologues of N2O would cause spectral shifts leading to isotopic fractionation of N2O in the stratosphere, because differences in overlap of their spectra with the solar spectrum lead to differences in photolysis rates. Of particular interest was the prediction that 14N15N16O and 15N14N16O should have different vertical fractionation profiles. This paper spawned a flurry of laboratory photolysis studies and stratospheric measurements by both mass spectrometry on collected samples and infrared remote sensing. These collected studies confirmed the fundamental correctness of the theory, although further consideration of excited vibrational states was required to explain temperature dependences and achieve better quantitative agreement between various levels of the-

ory and the measurements.

This paper presents ab initio theoretical calculations of these isotopic fractionation effects without use of empirical corrections. Theoretical predictions are compared to laboratory measurements as functions of wavelength and temperature for the most important isotopologues. In general the agreement is good and suggests that the postulated mechanism for isotopic fractionation is well understood. The paper provides a timely overview of the field and is well suited to publication in ACP. I recommend that it be published with the minor technical corrections and comments below.

P 16077

L15: "its" has no apostrophe here

L20: "... will significantly enrich the heavy isotopologues in the remaining N2O." For readers not familiar with N2O isotopic fractionation, one or two sentences here describing the basic mechanism in plain English would be very useful and make the introduction more readable.

P16078

L10: Please clarify the last sentence – do you mean that the Kaiser and Roeckmann study reduced the estimated contribution of the NH2 + NO2 reaction from 3% to 0.4%?

L18: ... the only one to be based ..."

L27: either "... nearly exact, and the calculated..." or .. "nearly exact. The calculated..."

P 16080

L1: please define TDM at first usage.

P16083 L11, eq. 5: A one or two line derivation of this important equation would be helpful.

P16089

L8: If the representation of the bandpass filter is poor, why not improve it? Is the filter bandpass spectrum known, If not, say so, if it is, why not redo this calculation with the correct shape?

P16090

L8: I suggest “mass independent oxygen isotope anomaly”.

Figure 6: This figure is hard to follow, could the caption be expanded to be more explicit in describing the three lines, crosses and triangles, and how the values of f relate.

Figure 7: Similarly, the figure would benefit from a more complete and specific caption

Yung, Y. L., and C. E. Miller (1997), Isotopic fractionation of stratospheric nitrous oxide, Science, 278, 1778-1780.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 16075, 2011.