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Interactive comment on "Wavelength dependence of isotope fractionation in N_2O photolysis" *by* J. Kaiser et al.

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Referee #1 refers to a typo on page 1741. However, the original paper is actually correct. As discussed in the quoted reference (Kaiser et al., 2002b), O(^1D) is most likely produced from NO_2 photolysis and then reacts with N_2O. The contribution of O(^1D) production from N_2O photolysis is not relevant and cannot account for the observed decrease in the magnitude of the fractionation constant towards higher degrees of conversion, since the N_2O mixing ratio is constantly decreasing. In contrast, the photochemical product NO_2 is likely to build up in the reactor (Kaiser et al., 2002b).

We agree with referee #1 that in terms of stratospheric N_2O photolysis, enough effort has been put into studying the isotopic fractionation of N_2O. However, it may still be interesting to investigate the difference in absorption cross sections for different isotopically substituted N_2O species to get a deeper insight into the dynamics and underlying molecular properties of N_2O photodissociation.

James Donaldson comments that we assume a uniform quantum yield for N_2O photolysis and neglect any temperature dependence of the absorption cross section or quantum yield. Although this is true, it is of no relevance in the present case, since we only investigate relative absorption cross sections of $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$ and $^{14}N_2{}^{18}O$ to $^{14}N_2{}^{16}O$. In the absence of any other evidence, we rather assume that the quantum yield is the same for all isotopomers and isotopologues and therefore cancels out, so that the fractionation factor (defined as the reaction rate ratio of the N_2O species with the heavy isotope over that with the light isotope) can be identified with the ratio of absorption cross sections for both species. To our knowledge, no measurements of the quantum yield in N_2O photolysis of individual isotopically substituted N_2O species exist. Both the recent NASA-JPL (DeMore et al., 1997) and IUPAC (Atkinson et al., 2002) evaluations of kinetic reaction data recommend a quantum yield of 1 for O(^1D) production in N_2O photolysis. In any case, we need not worry about this assumption in the interpretation of stratospheric observations, since we would also observe the combined effects of changes in absorption cross section and quantum yield upon isotopic substitution. The temperature dependence of isotopic fractionation by N_2O photolysis has been adressed in a companion paper (Kaiser et al., 2002b). The present paper only presents measurements at room temperature. For clarity, we will address both the O(^1D) and temperature issues in the final version which will be submitted for publication in ACP.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 1735, 2002.

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