Geophysical Research Abstracts
Vol. 14, EGU2012-7317, 2012
EGU General Assembly 2012

Isotope effects in N_2O photolysis from first principles

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This work gives important new insight into the fundamental mechanism of isotopic fractionation in N_2O photolysis. For the first time, accurate potential energy surfaces allow N_2O cross sections and isotopic fractionation spectra to be derived that are in agreement with available experimental data without artificial scaling and shifting, extending knowledge to a much broader range of conditions. Absorption spectra of rare N and O isotopologues (^{15}NNO, N^{15}NO, ^{15}N^{15}NO, NN^{17}O and NN^{18}O) are compared to the most abundant isotopologue (NNO). The fractionation constants as a function of wavelength and temperature are in excellent agreement with experimental data. The study shows that excitations from the 3rd excited bending state, $(0, 3, 0)$, and the first combination band, $(1, 1, 0)$, are important for explaining the isotope effect at wavelengths longer than 210 nm. Only a small amount of the mass independent oxygen isotope anomaly observed in atmospheric N_2O samples can be explained as arising from photolysis.