Geophysical Research Abstracts
Vol. 16, EGU2014-7214, 2014
EGU General Assembly 2014

Isotope effects in photo dissociation of ozone with visible light

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Ozone (O_3) plays a key role for many chemical oxidation processes in the Earth's atmosphere. In these chemical reactions, ozone can transfer oxygen to other trace gases. This is particularly interesting, since O_3 has a very peculiar isotope composition. Following the mass dependent fractionation equation $\delta 17O = 0.52 * \delta 18O$, most fractionation processes depend directly on mass. However, O_3 shows an offset to the mass dependent fractionation line. Processes, which show such anomalies, are termed mass independent fractionations (MIF). A very well studied example for a chemical reaction that leads to mass independent fractionation is the O_3 formation reaction. To what degree O_3 destruction reactions need to be considered in order to understand the isotope composition of atmospheric O_3 is still not fully understood and an open question within scientific community.
We set up new experiments to investigate the isotope effect resulting from photo dissociation of O_3 in the Chappuis band (R1). Initial O_3 is produced by an electric discharge. After photolysis O_3 is collected in a cold trap at the triple point temperature of nitrogen (63K). O_3 is then converted to O_2 in order to measure the oxygen isotopes of O_3 using isotope ratio mass spectrometry.
To isolate O_3 photo dissociation (R1) from O_3 decomposition (R2) and secondary O_3 formation (R3), we use varying amounts of carbon monoxide (CO) as O atom quencher (R4). In this way we suppress the $O + O_3$ reaction (R3) and determine the isotope fractionation in R1 and R2 separately. We present first results on the isotope effects in O_3 photo dissociation with visible light in the presence of different bath gases. Results are interpreted based on chemical kinetics modeling.

(R1) $O_3 + h\upsilon \rightarrow O\,(3P) + O_2$
(R2) $O_3 + O\,(3P) \rightarrow 2\,O_2$
(R3) $O + O_2 + M \rightarrow O_3 + M$
(R4) $O\,(3P) + CO + M \rightarrow CO_2 + M$