

Laser Spectroscopic Study on Oxygen Isotope Effects in Ozone Surface Decomposition

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The isotope kinetics of ozone formation in the Chapman reaction [1]



provides the primary example for a chemically induced oxygen isotope anomaly and is associated with large [2] and mass independent [3] oxygen isotope enrichments in the product molecule, linked to a symmetry selection in the ozone formation kinetics [4–5]. The isotopic composition of ozone and its transfer to other molecules is a powerful tracer in the atmospheric and biogeochemical sciences [6] and serves as a primary model for a possible explanation of the oxygen isotopic heterogeneity in the Solar system [7–8]. Recently, the isotope fractionation in the photolytic decomposition process



using visible light has been studied in detail [9–10]. Much less is currently known about the isotope fractionation in the dry deposition or in the gas phase thermal decomposition of ozone



Here we report on first spectroscopic studies of non-photolytic ozone decomposition using a cw-quantum cascade laser at 9.5 μm . The concentration of individual ozone isotopomers ($^{16}\text{O}_3$, $^{16}\text{O}^{16}\text{O}^{17}\text{O}$, and $^{16}\text{O}^{17}\text{O}^{16}\text{O}$) in a teflon coated reaction cell is followed in real time at temperatures between 25 and 150 °C. Observed ozone decay rates depend on homogeneous (reaction (3)) processes in the gas phase and on heterogeneous reactions on the wall. A preliminary analysis reveals agreement with currently recommended ozone decay rates in the gas phase and the absence of a large symmetry selection in the surface decomposition process, indicating the absence of a mass independent fractionation effect. This result is in agreement with previous mass spectrometer (MS) studies on heterogeneous ozone formation on pyrex [11], but contradicts an earlier MS study [12] on ozone surface decomposition on pyrex and quartz. Implications for atmospheric chemistry will be discussed.

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