Anomalous isotopic enrichment in atmospheric trace gases: non-mass-dependent isotope effects in ozone formation

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Observations have shown that atmospheric O₃ is enriched in $^{17}$O and $^{18}$O relative to the O₂ from which it is photochemically produced. Typical observed values are in the range 7-11% for both $^{49}$O₃ and $^{50}$O₃ and thus the enrichments are said to be mass independent. This unusual oxygen signature can be transferred by photochemical exchange reactions to other atmospheric species, such as CO₂, and to dissolved O₂ in oceans and lakes. The isotope anomaly is being suggested as a tracer of stratospheric ozone production, upper stratosphere and mesosphere dynamics and gross carbon cycle fluxes in the troposphere. The isotope anomaly in dissolved O₂ can be applied as a tracer for biological productivity and air/sea exchange rates. The ozone enrichments are known to be temperature and pressure dependent and are attributed to the three-body recombination reaction of O₃. This O₃ recombination has become a benchmark reaction for investigating the isotopic dependence of the dynamics and kinetics of a three-body chemical reaction.

$$\text{O}^{(3P)} + \text{O}_2 + \text{M} \rightarrow \text{O}_3^{\text{hot}} + \text{M} \rightarrow \text{O}_2 + \text{M}^{\text{hot}}$$

While this isotope effect is far from fully understood, it has been suggested that the observed enrichment in O₃ arises from a combination of a statistical isotope effect which depends on the difference in zero-point energy between different isotopomers, and from a non-statistical effect which is primarily due to subtle, non-standard differences in the densities of states between symmetric and asymmetric isotopomers.

The research presented here explores the pressure and bath gas dependence of the isotopic enrichments arising from the O₃ formation reaction. The O₃ was formed by photolysis of O₂ in the presence of different bath gases (Ar, O₂, CO₂ and SF₆) and the final isotopic composition measured on an isotope ratio mass spectrometer. The measured concentrations and enrichments analyzed by kinetic modeling of reaction system. Further modeling investigates the pressure dependence of the anomalous isotope effect in O₃ and the transfer of this anomaly to CO₂.