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Effect of nuclear spin on oxygen isotopic exchange between CO_2 and $O(^1D)$

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The stratospheric CO_2 is anomalously enriched in heavy oxygen isotopes compared to the tropospheric CO_2. Several measurements have established the enrichment firmly and showed that the enrichment in ^{17}O is greater than that of ^{18}O by a factor of 1.2 to 2.1. It is also seen that the enrichment in ^{18}O and ^{17}O increases with increase in altitude while the value of the slope relating two enrichments ($\Delta(\delta^{17}O)$ vs. $\Delta(\delta^{18}O)$) decreases. It is proposed that the enrichment in CO_2 is due to an isotope exchange reaction between CO_2 and $O(^1D)$, the latter being produced by UV dissociation of ozone. It is well known that the stratospheric ozone is unusually enriched in heavy oxygen isotopes (70 to130 ‰ in ^{17}O and ^{18}O) relative to the ambient oxygen from which it is produced. As $O(^1D)$ is derived from ozone it also possesses this anomalous enrichment and transfers its heaviness to CO_2 during its interaction. However, it is not clear how ozone with slope ~1 transfers its heavy oxygen isotopes to CO_2 to make the slope greater than 1. The molecular level detail of the heavy oxygen isotope transfer from ozone to CO_2 is still lacking and we do not know if the $O(^1D)$-CO_2 exchange process is a simple transfer of the isotope anomaly from ozone to CO_2 or involves some other anomalous isotope effect associated with CO_3^* formation/dissociation.

Recently, Chakraborty and Bhattacharya [2003] have demonstrated a slope ~1.8 relating $\Delta(\delta^{17}O)$ vs.g$\Delta(\delta^{18}O)$ in a laboratory experiment involving isotope exchange between ozone and CO_2 which is similar to the value in lower stratosphere. We have used a chemical reaction model to simulate their experimental data. The comparison of model predicted and experimentally observed data shows that the enrichment observed in CO_2 cannot be explained by a simple exchange. To explain the observed

data it is necessary to invoke a mechanism which can enhance $^{17}O(^{1}D)$ exchange rate relative to $^{18}O(^{1}D)$ and $^{16}O(^{1}D)$. It is known that the $O(^{1}D)$-CO_2 exchange is a spin forbidden reaction and requires presence of spin-orbit coupling. We propose that the nuclear spin of ^{17}O adds an extra component in the total spin–orbit coupling term enhancing the exchange rate of $^{17}O(^{1}D)$. The data require a nuclear spin effect of nearly 12% relative to ^{18}O to give agreement with observed data. If true, this would be the first experimental demonstration of nuclear spin effect in isotope exchange.