Photochemical and dynamics studies of oxygen isotope exchange reactions of CO_2

Thesis by

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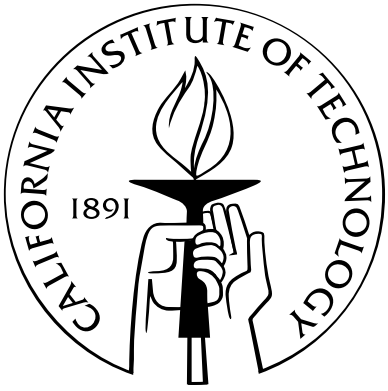

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Small quantities of different gases were added to separate portions of a non-inflammable mixture of dry carbonic oxide and oxygen, and the spark was then passed. In all cases where a gas containing hydrogen was introduced, the mixture exploded; in all cases where a gas containing no hydrogen was introduced, the mixture did not explode.

— Harold Dixon, *The Combustion of Carbonic Oxide and Hydrogen*, 1886.

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Abstract

This dissertation describes laboratory studies of three oxygen isotope exchange reactions — $O(^1D)$ + CO_2, O_2 + CO_2, and $O(^3P)$ + CO_2 — and their importance to oxygen cycling in the upper atmosphere. First, we studied the isotope exchange reaction $O(^1D)$ + CO_2, which is believed to govern the oxygen-isotope budget of CO_2 in the stratosphere. Our combined field, laboratory, and modeling study of the exceptionally rare $^{16}O^{13}C^{18}O$ isotopologue revealed that $O(^1D)$ + CO_2 explains only part of the stratospheric CO_2 isotopologue budget, not all of it as previously thought: $O(^1D)$ + CO_2 could not explain the large enrichments of $^{16}O^{13}C^{18}O$ (i.e., of the "Δ_{47}" tracer) at high Northern latitudes. Mesospheric and heterogeneous chemistry of CO_2 were proposed as possible sources of this meridional variation in $^{16}O^{13}C^{18}O$. Therefore, we performed crossed-molecular-beam experiments to investigate the chemistry of CO_2 at hyperthermal collision energies; this class of reaction could be important in the upper atmosphere, where low gas densities and high rates of photochemistry increase the relative probability of hyperthermal reactions. Our experimental and theoretical study of the O_2 + CO_2 isotope exchange reaction showed that the reaction can occur through a short-lived CO_4 reaction complex, which leads to O_2 + CO_2 products that are highly internally excited, but possibly still in their ground electronic state. Our study of $O(^3P)$ + CO_2 collisions at hyperthermal energies showed that $O(^3P)$ + CO_2 isotope exchange can occur in the upper atmosphere, proceeding through a short-lived CO_3 reaction complex. The $O(^3P)$ + $CO_2 \rightarrow O_2$ + CO reaction was also observed, and our data suggest that it can proceed through a 'stripping' mechanism or a CO_3 complex. These reactions demonstrate new ways in which oxygen can be cycled through CO_2 in the atmosphere; their isotope effects, manifest in the isotopic composition of atmospheric CO_2, may impose independent constraints on atmospheric transport and biosphere-atmosphere interactions.

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