

DIRECT MEASUREMENT OF $\text{OD}+\text{CO}\rightarrow \text{cis-DOCOCO}$, trans-DOCOCO , AND $\text{D}+\text{CO}_2$ BRANCHING KINETICS USING TIME-RESOLVED FREQUENCY COMB SPECTROSCOPY

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The kinetics of the reaction $\text{OH}+\text{CO}\rightarrow\text{H}+\text{CO}_2$ has attracted experimental and theoretical studies for more than 40 years due to its importance in atmospheric and combustion environments. This reaction proceeds on a rich potential energy landscape, first by forming vibrationally excited HOCO^* ; subsequently, HOCO^* either back reacts to $\text{OH}+\text{CO}$, dissociates to $\text{H}+\text{CO}_2$, or is stabilized to ground state HOCO by collisions with a third body. Due to the formation of the HOCO intermediate, the rate coefficient displays anomalous temperature and strong pressure dependences. Time-resolved Frequency Comb Spectroscopy (TRFCS) combines a mid-IR mode-locked femtosecond laser, a broadband optical enhancement cavity, and spatially dispersive detection system to simultaneously provide broad spectral bandwidth, high spectral resolution, high absorption sensitivity, and microsecond time resolution. We have applied this powerful technique to identify the deuterated analogues of HOCO isomers, trans-DOCOCO and cis-DOCOCO , for the first time in the reaction $\text{OD}+\text{CO}$ under ambient conditions. By directly monitoring the concentrations of OD (reactant), trans-DOCOCO , cis-DOCOCO (intermediates), and CO_2 (product), we unambiguously measure all pressure-dependent branching rates of the $\text{OD}+\text{CO}$ reaction.