

Laboratory Measurement of $\text{OH}(X^2\Pi_i, \nu \leq 4)$ Collisional Deactivation by Oxygen Atoms

The fluorescence of vibrationally excited, ground electronic state hydroxyl radical (OH) is one component of the terrestrial nightglow, originating in the mesopause-lower thermosphere region of the earth's atmosphere (~80–100 km). Hydroxyl radicals in $\nu = 6-9$ are formed in the reaction of hydrogen atoms with ozone, which in turn populate lower vibrational levels through collisions with molecular oxygen. The lifetimes of the lower levels ($\nu \leq 4$) are largely determined by collisions with atomic oxygen, as those with molecular oxygen are much less efficient at deactivation. Given the importance of O-atom collisions, we have developed an experimental approach and performed experiments on the collisional removal of $\text{OH}(\nu \leq 4)$ by atomic oxygen.

In this work, the reaction of OH with O-atoms are studied using a two-laser method. Reactants are generated by the photolysis of ozone in nitrogen with a pulsed excimer laser at 248 nm. A small fraction of the product $\text{O}(^1\text{D})$ reacts with either hydrogen to form $\text{OH}(\nu \leq 4)$ or with water vapor to form $\text{OH}(\nu \leq 2)$. The remainder of the $\text{O}(^1\text{D})$ is rapidly deactivated to produce ground state O-atoms. A second, time-delayed tunable dye laser pulse probes the OH population in a specific rovibrational state as a function of reaction time, using laser induced fluorescence in the $A^2\Sigma^+ - X^2\Pi_i$ system. By adjusting the composition of the reactant gas mixture and by varying the 248 nm laser fluence to control the ozone dissociation fraction, the dominant relaxation partner can be varied systematically from ozone and water or hydrogen to atomic oxygen.

Experimentally determined rate constants for the removal of $\text{OH}(\nu \leq 4)$ with oxygen atoms will be presented, comparing our values with other laboratory results and theoretical predictions. We find that for low vibrational levels ($\nu \leq 2$) our measurements are approximately a factor of three slower than the single previous, indirect measurement of the relaxation rate constant for $\nu = 1$. Preliminary measurements of $\text{OH}(\nu = 4)$ relaxation show a marked increase in the rate constant compared to that of $\text{OH}(\nu = 2)$. Experiments addressing the competition between reactive removal and vibrational energy transfer also will be presented with a preliminary elucidation of the relaxation mechanism. The significance of these measurements for the modeling of atmospheric nightglow emissions will be discussed.

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