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Laboratory Investigation of Relaxation Pathways for Vibrationally Excited OH

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The hydroxyl radical is a key species in the energy budget of the terrestrial atmospheres. In the Earth's upper atmosphere, vibrationally excited OH radicals ($v \leq 9$) are formed by the H + O_3 reaction. The non-thermal vibrational energy is either emitted as an infrared (IR) or visible photon, or converted into translational and internal energy via collisions with ambient gases. OH emission was recently reported for the first time in the nightglow of Venus [1]. Model calculations of the Mars airglow have also shown that the predicted intensity of the OH emission is extremely sensitive to the pathway of vibrational relaxation [2].

Accurate rate constant and mechanistic pathway information for the deactivation of the OH(v) states is essential in the modeling of both the atmospheric OH emission and the heating efficiency of the H + O_3 reaction, as exemplified in our studies of vibrational relaxation for OH(v = 7, 9) by O, O_2, N_2, and CO_2 [3,4].

We have initiated a research program to investigate the key pathways involved in OH(v) vibrational relaxation and their dependence on the collider species and temperature. In the laboratory experiments, we probe the fraction of collisions that lead to single-quantum relaxation of OH(v = 8) to OH(v = 7) for different atmospheric colliders. We developed a three-laser approach using the following steps: (1) generation of OH($v \leq 4$) by the O(^1D) + H_2 reaction following ozone photolysis at 248 nm by an KrF excimer laser in a mixture containing nitrogen and hydrogen; (2) infrared overtone excitation of the OH(v = 4) radicals to v = 7 at 938 nm using a pulsed optical parametric oscillator system triggered when the v = 4 population is near maximum and; (3) detection of the OH(v = 7) population by laser-induced fluorescence using the $B - X$ (0,7) band at 213 nm with a pulsed tunable dye laser timed in order to scan the delay with respect to the IR pump laser.

We will present the experimental methodology and measurements on the relaxation of OH(v = 8) to OH(v = 7) by O atoms and CO_2. Our measurements to date indicate that different collider gases favor distinct relaxation pathways: the single-quantum cascade branching ratio for collisions with CO_2 is approximately 3 times larger than that for collisions with O atoms. We will also discuss the atmospheric implications of our results based on the most current modeling calculations.

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