TEMPERATURE DEPENDENCE OF THE VIBRATIONAL RELAXATION OF OH(v = 1, 2) BY O, O_2, AND CO_2

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The hydroxyl radical is a key reactant in the energy budget of the atmospheres of terrestrial planets. In the Earth′s upper atmosphere, OH($v \leq 9$) is formed by the H + O_3 reaction. Recently, OH(v = 1 and 2) emission has been observed in the atmosphere of Venus.[a] The magnitude of this emission is controlled by the competition between radiative decay and vibrational relaxation by the most abundant collider, CO_2. The data needed to model the emission rates of vibrationally excited OH radical include the vibrational quenching rates at temperatures relevant to the planetary atmospheres and the branching ratio between single- and multi- quantum relaxation steps. The latter parameter plays a crucial role in establishing the emission rates, as demonstrated by recent model calculations. [b]
Given the importance of rate constants and branching ratios for understanding the behavior of atmospheric OH on both Earth and Venus, we applied a two-laser approach to measure the rate constants for the vibrational relaxation of OH(v = 1, 2) by O-atoms, O_2, and CO_2. In these experiments, ozone is almost completely photolyzed at 248 nm and most of the resulting O(^1D) atoms quenched to O(^3P) by collisions with N_2 and CO_2. A small fraction of O(^1D) reacts with H_2O, forming OH($v \leq 2$). The temporal evolutions of OH(v = 1, 2) are measured using laser induced fluorescence and kinetic simulations are used to extract the rate constants and the relaxation branching ratios. Experiments were performed at temperatures between 210 and 300 K. We find that the collisional removal rate constants for OH(v = 2) increase as the temperature decreases. The CO_2 branching ratio indicates that most of OH(v = 2) relaxes to OH(v = 1) following collisions with CO_2, i.e., the cascading removal pathway is predominant.

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[a] G. Piccioni *et al.*, Astronomy & Astrophysics, **483**, L29 (2008)
[b] A. G. Garcia-Muñoz *et al.*, Icarus, **176**,75 (2005); X. Zhu and J. H. Yee, Icarus, **189**, 136 (2007)