SPECTROSCOPIC CHARACTERIZATION OF HIGHLY PREDISSOCIATIVE LEVELS OF THE OH $A\,^2\Sigma^+$ STATE

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The OH radical plays a major role in atmospheric and combustion environments, where it is generally detected by Laser Induced Fluorescence (LIF) using the $A\,^2\Sigma^+ - X\,^2\Pi$ band system. Excited vibrational levels of the OH $A\,^2\Sigma^+$ $(v \geq 3)$ state have been difficult to study by LIF due to rapid predissociation, which results in a fluorescence quantum yield that is essentially zero. In the present work, the OH $A\,^2\Sigma^+$ $(v = 4)$ state is characterized using a Fluorescence Depletion Infrared (FDIR) spectroscopy technique. A UV laser promotes OH radicals from the $v'' = 1$ level of the ground $X\,^2\Pi$ state to the $v' = 2$ level of the excited $A\,^2\Sigma^+$ state. An IR laser further excites the OH radicals on an overtone transition to the $v = 4$ level of the $A\,^2\Sigma^+$ state. Fluorescence is collected from OH $A\,^2\Sigma^+$ $(v' = 2)$ exclusively, which is depleted when the IR laser is resonant with a $4 \leftarrow 2$ overtone transition. The IR frequencies of various P- and R-branch lines of the overtone transition are measured, and spectroscopic constants for the $A\,^2\Sigma^+$ $(v = 4)$ state are extracted using combination differences. The rotational, centrifugal distortion, and spin-rotation constants are determined, along with the vibrational frequency for the overtone transition. These constants are compared with calculated values from Dunham coefficients for the OH $A\,^2\Sigma^+$ state and a merged fit of experimental data from previous studies.