EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE AlH $b^3\Sigma^- - a^3\Pi$ ELECTRONIC TRANSITION

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The laser fluorescence excitation spectrum of the $b^3\Sigma^- - a^3\Pi$ (0,0) band of AlH and AlD is reported. The AlH/AlD ($a^3\Pi$) state was prepared in a free-jet supersonic expansion by reaction of photolyzed trimethylaluminum with hydrogen or deuterium. Spectroscopic constants for the upper and lower vibronic levels were derived from fits to the measured transition wave numbers of the rotational lines. Lifetimes of $J' = 1$ rotational/fine-structure levels of electronically excited AlH/AlD($b^3\Sigma^-$,v'= 0) were determined from fluorescence decay waveforms with laser excitation on isolated rotational lines. The measured lifetimes were compared with values obtained in a theoretical treatment of the excited-state decay dynamics, wherein both radiative decay to the $a^3\Pi$ state and nonradiative decay through the repulsive $1^3\Sigma^+$ state were considered. The experimental and theoretical lifetimes are in good agreement. The theoretical treatment shows that the nonradiative excited-state decay dominates over radiative decay. The observed fine-structure dependence of the lifetimes results is due to the nature of the spin-orbit coupling of the $b^3\Sigma^-$ state with the $1^3\Sigma^+$ continuum.