Vibrational energy levels and predissociation lifetimes of the $A^2\Sigma^+$ state of SH/SD radicals by photodissociation spectroscopy

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Photo-predissociation of SH and SD radicals in the $A^2\Sigma^+$ state are investigated using the high-*n* Rydberg atom time-of-flight (HRTOF) technique. By measuring the photoproduct translational energy distributions as a function of excitation wavelength, contributions from overlapping $A^2\Sigma^+$ (v') ← $X^2\Pi$ (v'') transitions can be separated, and the H/D + S(^3P_J) photofragment yield (PFY) spectra are obtained across various rovibrational levels (SH v' = 0-6 and SD v' = 0-8) of the $A^2\Sigma^+$ ← $X^2\Pi$ bands. The upper $A^2\Sigma^+$ state vibrational levels v' = 5-6 of SH and v' = 3-8 of SD are determined for the first time. The PFY spectra are analyzed with the simulation program PGOPHER [1], which gives vibration origins and linewidths of the rovibrational levels of the $A^2\Sigma^+$ state. The broad linewidths (≥ 1.5 cm^{-1}) of the SH v' = 3-6 and SD v' = 2-6 and 8 states are observed for the first time in this work, demonstrating that these levels undergo rapid predissociation with lifetimes on the order of picosecond. The lifetimes of the SD v' = 0, N' = 1 and 2 levels are determined to be ~ 200 ns by pump-probe delay measurements. The experimentally measured lifetimes are in reasonable agreement with the theoretical predictions.

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