

SPECTROSCOPY AND PREDISSOCIATION DYNAMICS OF SH RADICALS VIA THE $A^2\Sigma^+$ STATE

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The spectroscopy and predissociation dynamics of several vibronic levels ($v' = 0-6$) of the SH $A^2\Sigma^+$ state have been studied using the high- n Rydberg atom time-of-flight (HRTOF) technique. By measuring the product translational energy distributions as a function of excitation wavelength, the H + S(3P_J) photofragment yield (PFY) spectra are obtained across the various $A^2\Sigma^+ \leftarrow X^2\Pi$ bands. The PFY spectra of the $A^2\Sigma^+ v' = 3-6$ states exhibit broad linewidths ($> 4 \text{ cm}^{-1}$), indicating that these levels undergo rapid predissociation with lifetimes on the order of picosecond. The measured spin-orbit branching fractions of the H + S($^3P_{J=2,1,0}$) product channels provide insights to the predissociation dynamics of the $A^2\Sigma^+$ state, which change dramatically as the vibrational level v' increases. The $A^2\Sigma^+ v' = 0$ state of SH predissociates mainly through adiabatic coupling to the $^4\Sigma^-$ repulsive state, while all three repulsive states ($^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$) are involved in the dissociation pathways for higher vibrational levels.