IS THE HCCS RADICAL LINEAR IN THE EXCITED STATE?

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The $\tilde{A}^2\Pi$ - $\tilde{X}^2\Pi$ 415 nm band system of the linear HCCS radical has been known since 1978, but the vibronic structure in this complex spectrum, which has both spin-orbit and Renner-Teller complications, has never been satisfactorily assigned, despite serious experimental and theoretical efforts. In a further attempt to understand the spectrum, we have studied the laser-induced fluorescence spectra of jet-cooled HCCS and DCCS, produced from thiophene precursors using the discharge jet technique. The 0_0^0 bands of HCCS and DCCS have been rotationally analyzed, providing precise ground and excited state spin-orbit splittings. The energy levels of the $v' = 0$ $^2\Pi_{3/2}$ component of DCCS are found to be perturbed by a very low-lying $^2\Sigma$ vibronic level, indicating that the HCC bending mode Renner-Teller effect is much larger than predicted by ab initio calculations with a linear excited state geometry. With this observation, the vibronic bands in the spectra of both isotopomers have been consistently assigned for the first time. Model calculations show that the large Renner-Teller effect and substantially different HCCS and DCCS excited state zero-point spin-orbit splittings can be explained with the assumption of a quasilinear excited state geometry.