RENNER-TELLER VIBRONIC ANALYIS OF THE GROUND STATE ENERGY LEVELS OF THE HCCS FREE RADICAL

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We have studied the tetra-atomic Renner-Teller effect in the ground state of the jet-cooled HCCS and DCCS free radicals. The reactive intermediates were produced in a pulsed discharge jet using thiophene or deuterated thiophene precursors and the ground state vibronic energies were measured using the single vibronic level emission spectroscopy technique. In HCCS, emission and fluorescence depletion experiments proved that some previously unassigned LIF features were anomalous $^2\Delta_{3/2} -^2 \Pi_{3/2}$ transitions, which gave information on several ground state $^2\Delta_{3/2}$ levels. In DCCS, rotational mixing of the excited state v = 0 ($^2\Pi_{3/2}$) level with the 4^1 ($1^2\Sigma_{1/2}$) level allowed several ground state $^2\Sigma$ levels to be observed in emission. In addition, all of the expected $^2\Pi_{3/2}$ and the majority of the $^2\Pi_{1/2}$ levels up to 1700 cm^{-1} have been observed for both isotopomers. The data have been fitted by an effective Hamiltonian matrix treatment that included Renner-Teller, spin-orbit coupling, anharmonicity, and Fermi resonance effects for the two bending vibrations and the CS stretching mode. This has allowed an unusually complete description of the orbital angular momentum coupling effects, including the determination of the ϵ_4, ϵ_5, and ϵ_{45} terms for the first time. Subtle effects in both the LIF and emission spectra signal the presence of Sears resonances in both the ground and excited states of these radicals.