SUB-DOPPLER INFRARED SPECTROSCOPY OF JET COOLED HCCL DIRADICAL: THE CH STRETCH AND VIBRATIONAL COUPLING IN THE GROUND ELECTRONIC STATE

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Diradical carbenes have long been recognized as important intermediates in a range of chemical processes, with the carbene's chemical reactivity being sensitive to the particular ground-state electronic structure. We have undertaken an investigation of chlorocarbene (HCCl) by seeding $CHCl_3$ into a Ne/He/H_2 mixture and passing this mixture through a pulsed slit discharge. In the discharge environment, the $CHCl_3$ undergoes a double Cl atom removal process through a combination of electron dissociative attachment and hydrogen abstraction. The subsequent jet expansion cools the HCCl diradical to a 32 K rotational temperature. With the goal of assisting the search for HCCl chemistry in interstellar molecular clouds, the rotational constants for the ground singlet state of both the ^{35}Cl and ^{37}Cl isotopologues are determined through least-squares fits of ground-state combination differences to an asymmetric top Watson Hamiltonian. A Watson Hamiltonian is also used to extract rotational constants for the nominally (100) vibrationally excited state, with a highly mixed combination band (nominally (012), one quantum of H-C-Cl bend plus two quanta of C-Cl stretch) of comparable intensity found within a few wavenumbers (cm^{-1}) of the CH stretch band origin. The proximity of these two bands and the comparable infrared intensities of both combination and fundamental bands points towards a highly mixed state with strong anharmonic coupling between these two zeroth order modes. We quantify the anharmonic coupling in a 2x2 matrix deperturbation treatment and find it to be similar in magnitude to the previously measured spin-orbit coupling constants between the singlet and nearby lying triplet manifold of states.