LOW-LYING ELECTRONIC STATES OF C_4H: NOT SIMPLE

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The C_4H molecule is of significant astronomical interest. It represents one of the smallest "carbon chain" radicals, is abundantly distributed in astronomical sources, and C_4H^- was the one of the first molecular anions to be detected in space. The acetylenic radicals $H(C_2)_n$ form an interesting sequence in which low-lying excited electronic states are conspicuous. The simplest radical (C_2H) has a $^2\Sigma$ ground state, with the $^2\Pi$ excited state just below 0.5 eV higher. As the length of the carbon chain increases, the delocalization present in the $^2\Pi$ state (relative to $^2\Sigma$, which is acetylenic in nature with the unpaired spin localized on the terminal carbon) leads to its preferential stabilization, and $^2\Pi$ lies comfortably below $^2\Sigma$ for C_6H and larger members of the series. In this regard, C_4H sits essentially on the frontier: the most recent experiments place the $^2\Sigma$ lowest, but by only $<$30 meV, and a clear picture of its low-level vibronic level structure has yet to emerge. This talk discusses all three of the low-lying states ($^2\Sigma$ and the two components of $^2\Pi$), which in fact display a low-lying three-state conical intersection within 150 meV of the minimum on the adiabatic surface, and undergo profound vibronic pseudo-Jahn-Teller ($^2\Sigma/^2\Pi$) and Renner-Teller ($^2\Pi$) mixing. High-level calculations are performed to identify the various principal stationary points and conical intersections on the potential, and this information is used to construct a three-state vibronic Hamiltonian of the Köppel-Cederbaum-Domcke variety. These results are used to present a view of the electronic structure of this molecule that goes beyond the simple description of simple $^2\Sigma$ and Renner-Teller distorted $^2\Pi$ states that has typically been invoked in the past, and to carry out a simulation of the photoelectron spectrum.