

ROTATIONAL SPECTRA AND AB INITIO THEORY OF THE SILACUMULENE CHAINS $\text{H}_2\text{C}_n\text{Si}$

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The silacumulene chains $\text{H}_2\text{C}_n\text{Si}$ have been the subject of study by molecular beam Fourier transform microwave spectroscopy and *ab initio* calculation by coupled cluster methods. Each chain is predicted to possess a singlet electronic ground state, and a linear heavyatom backbone with two equivalent off-axis H atoms. Equilibrium structures and dipole moments for chains up to $\text{H}_2\text{C}_8\text{Si}$ were derived from large-scale CCSD(T) calculations. The rotational spectra of two chains, H_2CCSi and $\text{H}_2\text{C}_4\text{Si}$, have now been detected in the laboratory, and precise spectroscopic constants were derived for each molecule. For H_2CCSi , an experimental structure has been determined to high accuracy by isotopic substitution. In addition, rotational transitions between $K_a = \pm 1$ levels of the ^{29}Si and the two ^{13}C isotopic species of H_2CCSi exhibit nuclear spin-rotation hyperfine structure owing to the abnormally large component of the nuclear spin-rotation tensor along the a -inertial axis.