THE OPTICAL SPECTRUM OF THE SILICON TERMINATED CARBON CHAINS SiCnH

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The gas phase optical spectra of the silicon terminated carbon chains, SiC_nH (n=3-5) formed in a silane acetylene discharge, have been investigated by R2C2PI and LIF/DF and will be reported here for the first time. Complementary to the experimental work, a theoretical investigation was undertaken with coupled cluster methods to garner a comprehensive understanding of the molecular structures and electronic properties of these systems. For the linear chains where there is an odd number of carbon atoms (SiC_3H and SiC_5H), the observed transitions are primarily from a $^2\Pi$ ground state to a $^2\Sigma$ state, but as in the case of isovalent carbon chains there are some Herzberg-Teller active modes from an excited $^2\Pi$ state. While a strong $\Pi - \Pi$ transition is predicted for SiC_4H, the spectrum is dominated by relatively dark sigma state which is vibronically coupled to the bright $^2\Pi$ state. In contrast to the odd carbon chains, which exhibit relatively sharp spectral features and lifetimes in the 10-100 ns regime, SiC_4H shows broadened spectral features consistent with a ca. 10 ps lifetime, and a subsequent long-lived decay (> 30 microseconds) which we tentatively interpret in terms of mixing with a nearby quartet state arising from the same electronic configuration, a process unavailable for the odd chains.