ROTATIONAL SPECTRA OF THE FREE RADICALS $C_{10}H$, $C_{12}H$, $C_{13}H$, AND $C_{14}H$ IN A SUPERSONIC JET

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Four new carbon chain radicals $C_{10}H$, $C_{12}H$, $C_{13}H$, and $C_{14}H$ have been observed in a pulsed supersonic molecular beam with a Fourier transform microwave spectrometer. The radicals were produced in a discharge through a dilute diacetylene/neon mixture in the throat of a supersonic nozzle. All are found to be linear with $^2\Pi$ electronic ground states, and all except $C_{14}H$ have resolved lambda-type doubling. At least 10 rotational transitions, between 6 and 16 GHz, were measured in the lowest spin component — $^2\Pi_{3/2}$ of $C_{10}H$, $C_{12}H$, and $C_{14}H$, and the $^2\Pi_{1/2}$ component of $C_{13}H$. Only three spectroscopic constants in the standard Hamiltonian for a molecule in a $^2\Pi$ state were required to reproduce the spectra to a few parts in 10^7: an effective rotational constant, a centrifugal distortion constant, and a lambda-type doubling constant. Detection of these highly unsaturated carbon chains establishes that C_nH radicals containing up to 14 carbon atoms are readily produced in a supersonic molecular beam. The relative abundance of C_nH radicals with an *even* number of carbon atoms is fairly constant from C_6H through $C_{12}H$. Although the new radicals are about two orders of magnitude less abundant than C_4H, the strong predicted $^2\Pi -^2 \Pi$ electronic transitions may be detectable in a supersonic jet by standard laser spectroscopic techniques.