SUB-DOPPLER INFRARED SPECTROSCOPY OF JET COOLED BENZYl $\mathrm{C_6H_5CH_2}$: A CLASSIC RESONANTLY STABILIZED ORGANIC HYDROCARBON RADICAL

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The benzyl radical ($\mathrm{C_6H_5CH_2}$) is a classic example of a relatively long lived, resonantly stabilized transient molecule. Its relative stability makes it a likely intermediate in the formation of polycyclic aromatic hydrocarbons and ultimately soot during the combustion of fossil fuels. Benzyl radical is also thought to be candidate for detection in interstellar molecular clouds. Benzyl radical is generated by seeding benzyl chloride in a rare gas He/Ne mixture through a pulsed slit discharge, with the radical formation process likely dominated by electron dissociative attachment. The radicals are subsequently cooled in a slit jet supersonic expansion to a 15K rotational temperature. Narrow band infrared radiation is produced through difference frequency generation of two single-mode visible lasers. High frequency stability ($\pm 11\,\mathrm{MHz}$) is achieved through servo-locking techniques, and meticulous suppression of noise permits detection sensitivities approaching the quantum shot-noise limit. The slit jet has an inherent sub-Doppler resolution of 60 MHz. The present work reports the first ro-vibrationally resolved infrared spectra of antisymmetric (ν_3, $\mathrm{B_2}$) and symmetric (ν_4, $\mathrm{A_1}$) CH ring stretch modes in benzyl radical, with band origins ($3073.2350 \pm 0.0005\,\mathrm{cm^{-1}}$ and $3067.0576 \pm 0.0006\,\mathrm{cm^{-1}}$, respectively) and rotational constants determined by least-squares fits to an asymmetric top Hamiltonian. Surprisingly, the benzyl spectrum shows little evidence of dark-state perturbations despite the relatively large number of atoms ($\mathrm{N} = 14$) in this molecule. This is most likely due to the highly delocalized resonance structure of the benzyl radical, which generates a large barrier ($\Delta\mathrm{E} = 11.5\,\mathrm{kcal/mol}$) for internal rotation of the methylene group, suppresses the rovibrational density of states, and makes the tunneling splittings too small to detect with the present sub-Doppler resolution. Particular effort is directed toward accurate determination of the ground state rotational constants, with a goal of assisting microwave search for benzyl radical in the interstellar medium.