HIGH RESOLUTION ROVIBRATIONAL SPECTROSCOPY OF JET-COOLED PHENYL RADICAL: THE $\nu_{19}$ OUT-OF-PHASE SYMMETRIC C-H STRETCH

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Phenyl radical has been studied via sub-Doppler infrared spectroscopy in a slit supersonic discharge expansion source, with assignments for the highest frequency $b_2$ out-of-phase C-H symmetric stretch vibration ($\nu_{19}$) unambiguously confirmed by $\leq 6$ MHz (0.0002 cm$^{-1}$) agreement with microwave ground state combination differences of McMahon et al. [Astrophys. J. 590, L61-64 (2003)]. Least squares analysis of $>100$ resolved rovibrational peaks in the sub-Doppler spectrum to a Watson Hamiltonian yields precision exited-state rotational constants and a vibrational band origin ($\nu_0 = 3071.8915(4)$ cm$^{-1}$) consistent with a surprisingly small red-shift (0.9 cm$^{-1}$) with respect to Ar matrix isolation studies of Ellison and coworkers [J. Am. Chem. Soc. 123, 1977 (2001)]. Nuclear spin weights and inertial defects confirm the vibrationally averaged planarity and $^2A_1$ rovibronic symmetry of phenyl radical, with analysis of the rotational constants consistent with a modest $C_2v$ distortion of the carbon backbone frame due to partial sp rehybridization of the $\sigma$ C radical-center. Most importantly, despite the number of atoms (N = 11) and vibrational modes (3N$-6 = 27$), phenyl radical exhibits a remarkably clean jet cooled high resolution IR spectrum that shows no evidence of intramolecular vibrational relaxation (IVR) phenomena such as local or non-local perturbations due to strongly coupled nearby dark states. This provides strong support for the feasibility of high resolution infrared spectroscopy in other cyclic aromatic hydrocarbon radical systems.