HIGH RESOLUTION ROVIBRATIONAL SPECTROSCOPY OF JET-COOLED PHENYL RADICAL: THE ν_{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 (ν_{19}) unambiguously confirmed by ≤ 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 (ν_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 σ 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.