ELECTRONIC STRUCTURE OF PROTOTYPICAL π- and σ-RADICALS: HYPERFINE-RESOLVED ROTATIONAL SPECTROSCOPY OF PROPARGYL AND PHENYL

BRYAN CHANGALA, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; PETER R. FRANKE, *Department of Chemistry, University of Florida, Gainesville, FL, USA*; JOHN F. STANTON, *Quantum Theory Project, University of Florida, Gainesville, FL, USA*; BARNEY ELLISON, *Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA*; MICHAEL C McCARTHY, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*.

The reactivity of hydrocarbon radicals is strongly influenced by the orbital character and distribution of the unpaired electron. Hyperfine-resolved microwave spectroscopy is an ideal tool for measuring this structure in isolated, gas-phase molecules, providing fundamental insights into their open-shell electronic properties and chemical structure. We present examples of this approach applied to two prototypical reactive species: propargyl ($HCCCH_2$), the smallest resonance-stabilized π-radical, and phenyl (c-C_6H_5), the simplest aryl σ-radical. Using cavity Fourier transform microwave measurements of isotopically substituted propargyl, combined with highly accurate *ab initio* rovibrational corrections, we have derived its complete semi-experimental equilibrium structure and unpaired spin distribution, which provide vivid, complementary illustrations of π-electron delocalization. Our parallel work on phenyl has focused on the complete assignment of the complex hyperfine structure associated with its five ^{1}H nuclear spins. In addition to characterizing the singly occupied, carbon-centered σ-orbital, the precisely determined hyperfine parameters enable us to generate a kHz-accuracy cm-wave catalog. These laboratory data are an essential prerequisite for a sensitive astronomical search for phenyl in radio surveys of narrow-linewidth interstellar objects such as cold, dark molecular clouds, where phenyl is thought to be a critical intermediate in the formation of the first aromatic ring. Our work suggests that other large, weakly polar, open-shell hydrocarbons, including benzyl and indenyl, may be amenable to high-resolution microwave characterization.