THE RADIO SPECTRUM OF THE PHENYL RADICAL

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The phenyl radical, C_6H_5, derived from benzene by removal of one hydrogen, was detected at centimeter wavelengths in a pulsed supersonic molecular beam with a Fourier transform microwave spectrometer, and was subsequently observed in a low-pressure dc glow discharge with a free-space millimeter-wave spectrometer. Each rotational transition in the centimeter-wave band consists of many lines closely-spaced in frequency owing to the fine and hyperfine interactions from the unpaired electron and the five hydrogen atoms; owing to the collapse of this structure in the millimeter-wave band, the rotational spectrum greatly simplifies, allowing the most intense transitions in this region to be calculated to high accuracy. In all, 14 rotational transitions between 9 and 40 GHz and 62 transitions between 150 and 350 GHz have been measured for the normal isotopic species, and a comparable number have been measured for fully deuterated C_6D_5. Three rotational, three centrifugal distortion constants, and one spin-rotation constant reproduce the spectrum of both species at millimeter wavelengths to better than a few parts in 10^6. The spectroscopic constants are in excellent agreement with recent CCSD(T)/cc-pVTZ calculations, confirming that phenyl is a fairly rigid planar molecule with a small inertial defect comparable to that derived for benzene. Phenyl is an excellent candidate for astronomical detection because it is a fundamental reactive hydrocarbon species that is calculated to possess a dipole moment of 0.9 D.