CAVITY-RINGDOWN SPECTROSCOPY OF THE VIBRONICALLY MIXED $\tilde{A}\,^2A_2 - \tilde{B}\,^2B_2$ EXCITED STATES OF THE BENZYL RADICAL AND THE $\tilde{1}\,^2A_2 \leftarrow \tilde{X}\,^2B_1$ TRANSITION OF THE PHENOXY RADICAL IN A SUPERSONIC JET EXPANSION

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The benzyl and phenoxy radicals are hydrocarbon combustion intermediates that influence the formation of polyaromatic hydrocarbons (PAH's). By this means they impact the earliest stages of soot formation. Detection and characterization of the highly reactive intermediate species in PAH formation reactions can help us to describe the mechanisms involved. However, the low concentrations associated with these radicals require special detection techniques.

This study combines an electrical discharge to produce radicals, a supersonic jet expansion for collisional cooling, and utilizes cavity ringdown spectroscopy (CRDS) for detection. We report the absorption spectra for the vibronically mixed $\tilde{A}\,^2A_2 - \tilde{B}\,^2B_2$ excited states of the benzyl radical ($\approx$450nm) and the $\tilde{1}\,^2A_2 \leftarrow \tilde{X}\,^2B_1$ electronic transition of the phenoxy radical. Rotationally structure is somewhat resolved, and as such a contour fit was performed using the PGOPHER program. Rotational temperatures of 20 and 30 K were indicated for benzyl and phenoxy, respectively. Molecular constants were extracted using a least squares contour fitting procedure. Homogeneous line broadening was observed for phenoxy, and the excited state lifetime was estimated for various vibronic states. Summaries of the data for both radicals, along with comparisons to the results from electronic structure calculations, will be presented.