JET-COOLED EXCITATION SPECTRA OF LARGE BENZANNULATED BENZYL RADICALS: 9-ANTHRACENYLMETHYL ($C_{15}H_{11}$) and 1-PYRENYLMETHYL ($C_{17}H_{11}$)

GERARD D. O'CONNOR, GEORGE B. BACSKAY, GABRIELLE V.G. WOODHOUSE, TYLER P. TROY, KLAAS NAUTA, SCOTT H. KABLE and TIMOTHY W. SCHMIDT, *School of Chemistry, The University of Sydney, NSW 2006, Australia*.

The jet-cooled $D_1 \leftarrow D_0$ excitation spectra of two benzannulated benzyl radicals (BBRs), 9-anthracenylmethyl (9-AnMe) and 1-pyrenylmethyl (9-PyMe), have been obtained using mass-resolved resonant two-colour two-photon ionization spectroscopy (R2C2PI). Analysis of the spectra in view of symmetry and calculated vibrational frequencies indicate significant vibronic coupling. From the spectrum of 9-AnMe we elucidate significant anharmonicity in the excited state. This anharmonic behaviour is examined computationally through both TDDFT and *ab initio* methods. Excited state properties of 9-AnMe and 1-PyMe are examined with reference to the existing spectra of smaller BBRs. Trends in the observed spectra of BBRs allow spectroscopic properties of larger BBRs to be predicted. These predictions suggest the $D_1 \leftarrow D_0$ transitions of large BBRs are unlikely to be carriers of the diffuse interstellar bands.