THE ELECTRONIC SPECTRUM OF *PARA*-ETHYNYLBENZYL RADICAL

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Indenyl and phenylpropargyl are the most stable isomers of C_9H_7 and have emerged as ubiquitous products in flames and hydrocarbon discharges. Along with *ortho*-ethynylbenzyl, they are the only C_9H_7 isomers to have been spectroscopically studied in detail, but there presumably exists a wide variety of other resonance-stabilized C_9H_7 radicals that have not yet been detected. We report the observation of *para*-ethynylbenzyl radical, first found in a discharge of *para*-vinyltoluene during an unsuccessful search for *p*-vinylbenzyl, and subsequently observed with high signal-to-noise ratio when *p*-ethynyltoluene was used as the precursor. Identification of the radical is secured by comparison of the observed (7.17 eV) and calculated (7.08-7.25 eV) adiabatic ionization energy, and a convincing assignment of the electronic spectrum can be made from calculated excited state frequencies. The molecule adopts C_{2v} symmetry in its ground and first excited states. In almost every case where a single, strong a_1 fundamental is predicted in excitation, there exist two or more bright states in the spectrum. We attribute this to Fermi-resonance, a consequence of pervasive near-degeneracies of overtones of non-totally symmetric modes with Franck-Condon-active a_1 modes. Some instances have been confirmed by dispersed fluorescence spectroscopy at the time of writing. In addition, in the same *m/z* = 115 R2C2PI spectrum, we find unmistakable evidence of 1-phenylpropargyl, as well as the previously undetected *m*-ethynylbenzyl radical. Examination of the precursor by NMR proves that both radicals are present at levels that cannot be accounted for by sample impurities unless computed transition strengths are too small by several orders of magnitude, suggesting rearrangement of all three radicals *via* an intermediate that remains unobserved.