

## ELECTRONIC SPECTROSCOPY OF ETHYNYLBENZYL CHROMOPHORES

JONATHAN FLORES, SEDERRA D. ROSS, SIMA KHANI, MASSIMO RUSCITTI, DANIEL M. HEWETT, NEIL J. REILLY, *Department of Chemistry, University of Massachusetts Boston, Boston, MA, USA.*

The indenyl and phenylpropargyl radicals are the most stable isomers of  $C_9H_7$  and have emerged as ubiquitous products in flames and hydrocarbon discharges. The *o*-, *m*-, and *p*- ethynylbenzyl isomers lie *ca.* 150-160 kJ/mol and 20-30 kJ/mol above the 1-indenyl and 1-phenylpropargyl minima, respectively, and can presumably form by barrierless addition of CH radical to phenylacetylene, but they are thoroughly unexamined spectroscopically. We have recently observed the  $D_0 - D_1$  optical transitions of the *para* and *meta* variants by resonant two-color two-photon ionization and laser-induced fluorescence / dispersed fluorescence spectroscopy. For the *para* form, extension of the benzyl chromophore by a  $C_2$  unit engenders a relatively (w.r.t. benzyl) strong transition that can in large part be rationalized on Franck-Condon premises; while most of the vibronic structure in the much weaker transition of the *meta* isomer arises from intensity-borrowing among totally symmetric modes that are only weakly FC-active. Modes of  $a_1$  symmetry of *para*-ethynylbenzyl are subject to pervasive Fermi resonances, as is established by DF spectroscopy. In the jet-cooled discharge, both *para* and *meta* forms are found in coexistence with 1-phenylpropargyl (which one might call  $\alpha$ -ethynylbenzyl) at levels that cannot be explained by putative sample impurities unless computed oscillator strengths are too small by several orders of magnitude, suggesting rearrangement of all three radicals *via* an intermediate that remains unobserved. The *para* form has not been detected at the time of writing, perhaps because it cyclizes to indenyl.