ELECTRONIC SPECTROSCOPY OF *CIS*- AND *TRANS-META*-VINYLBENZYL RADICALS

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The electronic spectra of the resonance-stabilized radical C_9H_9 isomers *cis*- and *trans-meta*-vinylbenzyl (MVB), generated in a supersonically cooled discharge of *m*-vinyltoluene, have been investigated using resonant two-colour two-photon ionization (R2C2PI) and laser-induced fluorescence. The $D_0 - D_1$ band origins of the *cis* and *trans* conformers are at 19037 cm^{-1} and 18939 cm^{-1}, respectively. Adiabatic ionization energies near 7.17 eV were determined for both conformers from two-colour ion-yield scans. Dispersed fluorescence (DF) was used to conclusively identify the *cis* conformer: ground-state *cis*-MVB eigenvalues calculated from a Fourier series fit of a computed (B3LYP/6-311G++(d,p) vinyl torsion potential are in excellent agreement with torsional transitions observed in the 19037 cm^{-1} DF spectrum. Features arising from *cis*- or *trans*-MVB in the R2C2PI spectrum were distinguished by optical-optical holeburning spectroscopy and vibronic assignments were made with guidance from DFT and TDDFT calculations. There is a notable absence of mirror symmetry between excitation and emission spectra for several totally symmetric modes, whereby a' fundamentals that are conspicuous in emission are nearly absent in excitation, and *vice-versa*. This effect is largely ascribed to interference between Franck-Condon and Herzberg-Teller contributions to the electronic transition moment, as the former is carried with a different sign in excitation $vs.$ emission, while the latter is not. Rampant HT activity among a' modes is attributed to the low symmetry (C_s) of the molecule, which permits intensity-borrowing from several relatively bright electronic states of A'' symmetry.