CONFORMATIONALLY INDUCED TRANSITION MOMENT ROTATIONS IN THE $S_1 \leftarrow S_0$ ELECTRONIC SPECTRA OF JET-COOLED AROMATIC MOLECULES

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Fluorescence excitation and one-color resonant two-photon ionization spectra of jet-cooled n-propylbenzene, n-butylbenzene, phenylethylamine and phenylethylalcohol in the $S_1 \leftarrow S_0$ band origin region are presented. At least two monomer origin bands are observed in each spectrum, together with vibronic bands and cluster features. Partially resolved rotational contours of the monomer origin bands have been analysed with the aid of molecular orbital calculations conducted at the HF/6-31G* and CIS/6-31G* levels to provide structural assignments. The data show that different origin bands may be assigned to different conformes of the isolated molecule, distinguished by the orientation of the side chain with respect to the ring. Anti conformers display pure, b-type rotational band contours. Gauche conformers display hybrid structures, the composition of which shows that there is an electronically induced rotation of the optical transition moment in the inertial frame, which is sensitive to the nature and conformation of the substituent.