CONFORMATION-SPECIFIC INFRARED AND ULTRAVIOLET SPECTROSCOPY OF α-METHYLBENZYL RADICAL: PROBING THE STATE-DEPENDENT EFFECTS OF METHYL ROCKING AGAINST A RADICAL SITE

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Combustion processes involve a myriad of complex reaction pathways which connect smaller precursors to larger polyaromatic hydrocarbons, many of which are still unknown. In particular, benzyl-type radicals play an important role in combustible fuels due to their intrinsic resonance stabilization and consequent increase in relative concentration. Here, we present a study of the vibronic spectroscopy of α-Methylbenzyl radical (α-MeBz), in which the orientation of the methyl group adjacent to the radical site responds to the electronic interaction extending from the conjugated π-system. Probing the isolated radical, produced in an electrical discharge under jet-cooled conditions, the two-color resonant two-photon ionization, fluorescence excitation, and dispersed fluorescence spectra were obtained in order to determine the ground and excited state barriers to internal rotation and the angular change associated with electronic excitation. Resonant ion-dip infrared spectroscopy (RIDIRS) has also been implemented to elucidate the infrared signatures in the alkyl and aromatic CH stretch regions in order to probe in a complementary way the state-dependent conformational preferences of α-MeBz. We will show that the D_0- and D_1-RIDIR spectra report sensitively on the strong coupling between the CH stretch vibrations and the C_α-C_β torsional geometry. Furthermore, photoionization efficiency scans were carried out to reveal the adiabatic ionization threshold of α-MeBz and the quantized levels present in the radical cation state.