ANALYSIS OF THE VIBRONIC EMISSION SPECTRA OF JET-COOLED METHYL-SUBSTITUTED BENZYL RADICALS OBSERVED IN A CORONA EXCITED SUPERSONIC EXPANSION

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With a technique of corona excited supersonic expansion developed in this laboratory for the observation of vibronic emission spectra of transient molecular species, the jet-cooled dimethyl- and trimethyl-benzyl radicals were generated, respectively, from trimethyl- and tetramethyl-benzenes seeded in a large amount of inert carrier gas helium and vibronically excited in a jet using a pinhole-type glass nozzle. The well-resolved vibronic emission spectra of methyl- substituted benzyl radicals recorded with a long path monochromator in the D1-D0 transition show several strong vibronic bands originating from the vibrationless state of the two lowest excited electronic states, together with the origin bands of the pure electronic transitions. The observed bands have been analyzed to give the electronic transition and vibrational mode frequencies in the ground electronic state of the species by comparing with those from the bandshapes of three isomeric xylyl radicals as well as with those of ab initio calculation obtained using Gaussian 98 program for window package. The intensity analysis of two origin bands also provides the possible mechanism of the vibronic relaxation process occurring during the jet expansion.