

Vibronic spectroscopy of benzyl-type radicals using a technique of corona excited supersonic expansion.

Young Wook Yoon and Sang Kuk Lee
Department of Chemistry
Pusan National University
Pusan 609-735, Korea

The benzyl radical, a prototypical aromatic free radical, is believed to be an important intermediate in aromatic chain reactions and has been the subject of numerous spectroscopic works. On the other hand, benzyl-type radicals, ring-substituted benzyl radicals have received far less attention due to the difficulties associated with the identification of the species and possible rearrangement of substituents at the transition state.

In this laboratory, we developed the technique of corona excited supersonic expansion (CESE) for observation of vibronic emission spectra of benzyl-type radicals using a pinhole-type glass nozzle. Vibronically excited but jet-cooled benzyl-type radicals were generated from the corona discharge of the precursor, ring-substituted toluenes seeded in a large amount of inert carrier gas He, from which the visible vibronic emission spectra were recorded with a long-path monochromator. The spectra show the strongest origin band and were followed to red region by a series of vibronic band in the $D_1 \rightarrow D_0$ transition of the radicals.

From the analysis of the spectra observed, we identified the benzyl-type radicals formed in the corona discharge of the precursor and determined the electronic energy and several vibrational modes in the D_0 state to confirm the assignments of mono-substituted benzyl radicals by comparison with an *ab initio* calculation. For poly-substituted benzyl radicals, the origin band shows increased shift to red region due to the synergic effect of two substituents into benzene ring, the increased space for the delocalized π electrons on the molecular plane. The shift of the origin band of the most of the poly-substituted benzyl radicals is comparable to the summation of the contribution of each substituent depending on the kind and position of substituent. However, the poly-substituted benzyl radicals with substituent at the 4-position always show much smaller shift than others, for which we tried to explain the shift of the origin band using a simple molecular orbital theory. The new model describes well the shift of the origin band of the homo- and hetero-substituted benzyl-type radicals for CH_3 and F substituents.