SPECTROSCOPY OF BENZYL-TYPE RADICALS GENERATED BY ELECTRIC DISCHARGE : JET-COOLED DICHLOROBENZYL RADICALS

YOUNG WOOK YOON and SANG KUK LEE, *Department of Chemistry, Pusan National University, Pusan 609-735, Republic of Korea.*

The technique of corona excited supersonic expansion coupled with a pinhole-type glass nozzle has been proved a useful laser-free spectroscopic tool for observation of vibronic emission spectra of large aromatic molecules, especially for molecular radicals which are long believed to play an important role as a reaction intermediate in aromatic chemical reactions. The vibronic emission spectra recorded with a long-path monochromator exhibit the electronic transition energy in the $D_1 \rightarrow D_0$ transition and vibrational mode frequencies at the D_0 state. In this laboratory, all six isomeric dichlorobenzyl radicals[ab] have been produced from the corona discharge of corresponding dichlorotoluenes seeded in a large amount of inert carrier gas He. The vibronic emission spectra show very weak intensity due to the existence of Cl atoms in the precursor molecules and possible breakdown of benzene ring by free Cl atoms. Nevertheless, we clearly identified the origin band and a few well-known vibrational modes for each isomer. From an analysis of the spectra observed, we determined the energy of electronic transition and several vibrational modes in the ground electronic state. Also, the red-shift of the origin band from the parental benzyl radical clearly shows the substituent effect of Cl atoms on electronic energy, for which we satisfactorily explain in terms of the shape of the molecular planes and position of the nodal points at a given electronic state, recently developed in this laboratory for identification of isomeric multi-substituted benzyl-type radicals.

[a] Y. W. Yoon, C. S. Huh, and S. K. Lee, *Chem. Phys. Lett.* **550**, 58 (2012).
[b] S. K. Lee and S. J. Kim, *Chem. Phys. Lett.* **412**, 88 (2005).