

Vibronic Emission Spectroscopy of Jet-Cooled Benzyl-type Radicals Generated from Corona Discharge of Chloro-Substituted *o*-Xylenes

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Abstract: Jet-cooled but vibronically excited chloro-substituted methylbenzyl radicals were generated from corona discharge of precursors, chloro-substituted *o*-xylenes with a large amount of carrier gas helium in a technique of corona excited supersonic expansion. From the analysis of the spectra observed, we can identify each benzyl-type radical formed by comparing the observation with the ab initio calculation, from which the red-shift of the origin band of the chloro-substituted methylbenzyl radicals was explained in terms of the lowest occupied molecular orbital (LUMO).

Introduction: Whereas benzyl radical, a prototypic aromatic free radical, has been the subject of numerous spectroscopic studies, chloro-substituted benzyl radicals have received less attention, due to the difficulties associated with production of radicals from precursors. The weak C-Cl bond can be easily dissociated in corona discharge of high voltage, leading to the formation of other benzyl-type radicals. During past years, we have concentrated the spectroscopy of chloro-substituted methylbenzyl radicals produced from corona discharge of precursor seeded in a large amount of helium carrier gas using a pinhole-type glass nozzle in a technique of corona excited supersonic expansion.

Experiment: For the production of jet-cooled but vibronically excited benzyl-type radicals, we have employed a technique of corona excited supersonic expansion coupled with a pinhole-type glass nozzle which has been well developed in this laboratory. The precursors were vaporized in a glass vessel of 2 atom helium gas and undergone corona discharge of less than 2 kV during supersonic jet expansion. The weak green-blue emission was recorded to obtain the vibronic emission spectra shown in Fig. 1 using a long path monochromator (Jobin Yvon U1000).

Results and Discussion: From the analysis of the spectra observed, we obtained the spectroscopic data listed in Table 1 from the assignment of the origin band of each benzyl-type radical using the substituent effect on electronic transition energy, especially of orientation effect of substituents. The large and small red shifts were confirmed for the 5-chloro- and 3-chloro-*o*-methylbenzyl radicals, respectively. The elliptic shape of the molecular orbitals at the lowest unoccupied state agrees well

Table 1. Red-shifts of chloro-substituted-*o*-methylbenzyl radicals in the $D_1 \rightarrow D_0$ transition^a

Molecules	Origin band	Shift ^b	Difference ^c
3-chloro- <i>o</i> -methylbenzyl	20680	1322	143
4-chloro- <i>o</i> -methylbenzyl	21376	626	31
5-chloro- <i>o</i> -methylbenzyl	20270	1732	-267
6-chloro- <i>o</i> -methylbenzyl	20418	1584	35

^aMeasured in vacuum (cm^{-1}).

with the observation, leading to the understanding the orbital shape of delocalized π electrons shown in Fig. 2. We believe this is the first attempt to describe the orbital motion of delocalized π electrons on the benzene ring perturbed by substituents.

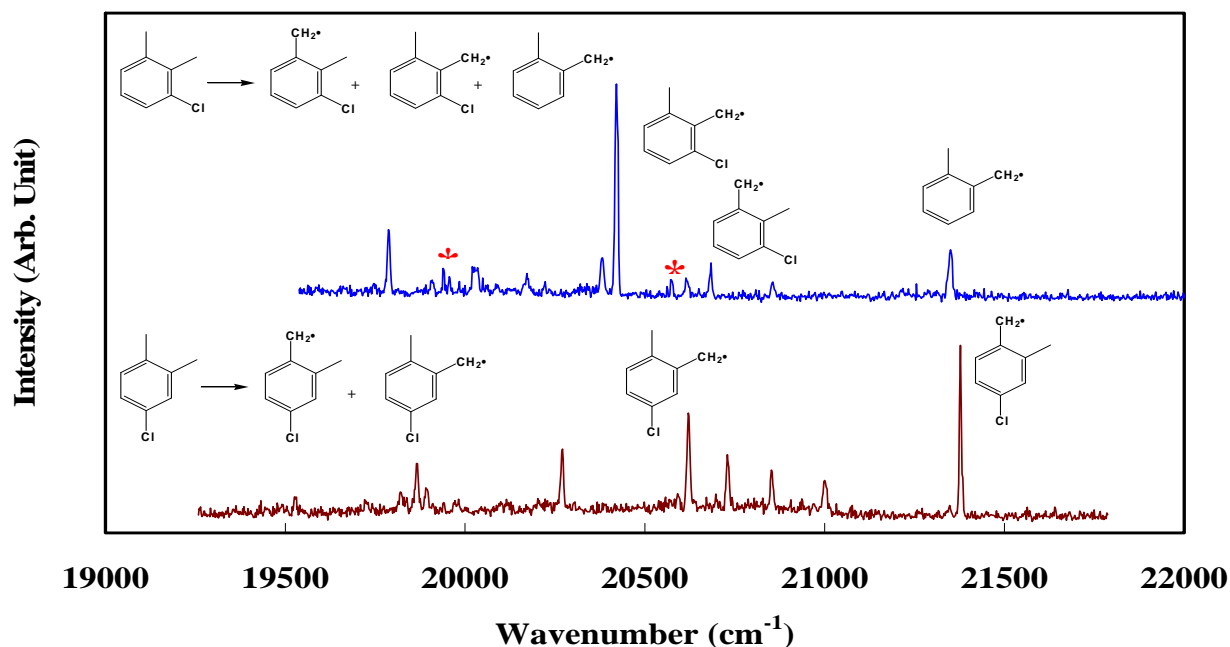


Figure 1. The vibronic emission spectra observed from the corona discharge of chloro-substituted o-xylene precursors seeded in a large amount of carrier gas helium. The top and bottom spectra were observed from 3-chloro-o-xylene and 4-chloro-o-xylene, respectively.

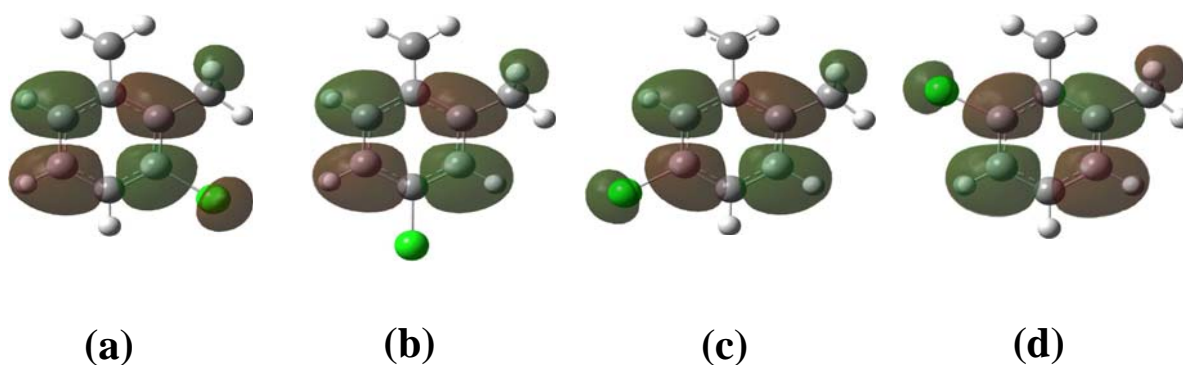


Figure 2. The 2-dimensional shape of lowest unoccupied molecular orbital of the chloro-substituted methylbenzyl radicals. The (a), (b), (c), and (d) represent the 3-chloro-, 4-chloro-, 5-chloro-, and 6-chloro-methylbenzyl radicals, respectively. The elliptic shape of molecular orbitals is believed to attribute to the size of red-shift of the origin band of the benzyl-type radical in the $D_1 \rightarrow D_0$ transition.