

# Vibronic spectroscopy of isomeric dimethylbenzyl radicals generated from 1,2,4-trimethylbenzene: Assignments and Substituent effect

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Benzyl radical, a prototypical aromatic free radical, has long been believed to play a key role in aromatic chain reactions and has been the subject of numerous spectroscopic studies. On the other hand, ring-substituted benzyl radicals, benzyl-type radicals, have attracted less attention due to the difficulties associated with the possible rearrangement of substituents at the transition state and analysis of spectra.

We applied the technique of corona excited supersonic jet expansion (CESE) to generate vibronically excited but jet-cooled dimethylbenzyl radicals from 1,2,4-trimethylbenzene precursor seeded in a large amount of carrier gas He using a pinhole-type glass nozzle developed in this laboratory, from which the visible vibronic emission spectra were recorded with a long-path double monochromator. The spectrum showed many vibronic bands of three isomeric dimethylbenzyl radicals, 2,4-, 2,5-, and 3,4-dimethylbenzyl radicals. However, the vibronic assignments could not be easily obtained due to the similarity of vibrational mode frequencies and electronic transition energy in the  $D_1 \rightarrow D_0$  transition among isomers.

The controversial vibronic assignments of isomeric dimethylbenzyl radicals were clearly resolved by employing corresponding dimethylbenzyl chlorides as precursors which can also produce dimethylbenzyl radicals by dissociation of C-Cl bond in corona discharge.

From the analysis of the spectra observed from the dimethylbenzyl chlorides in corona discharge, we revised the previous vibronic assignments of the radicals and determined the electronic energy in the  $D_1 \rightarrow D_0$  transition and vibrational mode assignments in the ground electronic state by comparing the observation with an *ab initio* calculation of radicals and with the known vibrational data of trimethylbenzenes.

In this presentation, we will discuss the details of observation of the spectra and vibronic assignments as well as the substituent effect<sup>1</sup> of methyl substitution on electronic transition energy which provides excellent basis for the assignments of multi-methylbenzyl radicals.

## References

- 1) Y. W. Yoon and S. K. Lee, *J. Chem. Phys.* **135**, 214305 (2011).