Communications

Observation of Jet-Cooled 2,6-Dichlorobenzyl Radical in a Corona Excited Supersonic Expansion

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Electronic structure of benzyl-type radicals with 7 delocalized π electrons has been the subject of numerous spectroscopic works.[1] Substitution in the benzene ring is also expected to affect the electronic energies and vibrational mode frequencies. Among mono-substituted benzyl-type radicals, the substitution at the *para* position has been examined more than the other isomers, since the transition dipole moments are parallel to the molecular symmetry axes, resulting in the characteristic bandshapes of the vibrational modes.[2]

Of many benzyl-type radicals, xylyl radicals[3-6] and fluoro-benzyl radicals[7-9] have been extensively examined because they emit strong fluorescence during the electronic transition, from which electronic energies and vibrational modes have been determined by using a variety of spectroscopic techniques. Recently, the visible vibronic emission spectra of the dimethyl-[10] and difluoro-[11] benzyl radicals were observed for the first time in this laboratory using a technique of a corona-excited supersonic expansion (CESE).

The 2,6-dichlorobenzyl radical is supposed to play an important role as a reaction intermediate in the formation of the most toxic chemical, dioxin, which is produced in the combustion process of chlorinated aromatic compounds in incinerators.[12] No spectroscopic work has been reported on this compound, probably due to the very weak fluorescence intensity in the visible region.

In this work, we report the formation of the jet-cooled 2,6-dichlorobenzyl radical for the first time, which was identified through the visible vibronic emission spectra. The origin band in the $D_1 \rightarrow D_0$ transition of the radical was compared with those of chlorobenzyl radicals as well as other types of benzyl radicals of similar structure..

Combination of jet expansion technique[13] with emission spectroscopy has significantly contributed to the spectroscopic development of molecular species that could not otherwise carried out. Among many emission sources developed for these purposes, the only one providing enough continuous photon intensity for high-resolution studies of the weak transition is a pinhole-type nozzle,[14-16] particularly for benzyl-type radicals in the gas phase.[17,18]

The technique of corona excited supersonic expansion has been employed to generate the 2,6-dichlorobenzyl radical that was produced in a jet from 2,6-dichlorotoluene (reagent grade, Aldrich) and vibronically excited with a large amount of inert carrier gas He of 2.0 atm during the expansion through the pinhole-type glass nozzle ($\varphi = 0.3$ mm). The concentration of vapor in the carrier gas was adjusted for the maximum emission intensity monitored from the strongest origin band by controlling the sample temperature and opening the by-pass valve of the carrier gas. The excitation was obtained using a high-voltage dc power supply in the negative polarity, in which the axial discharge current was 3-5 mA at 2000 V dc potential and stabilized using a 150 kΩ current limiting ballast resister. A green-colored jet was the evidence of the presence of the 2,6-dichlorobenzyl radicals in the jet.

It has been known that the benzyl-type radicals generated in a corona excitation will experience stepwise collisional relaxation during the expansion process, from which rovibrationally cold but electronically excited molecules will be formed.[19] Then, the molecules in the jet lose its electronic energy by emitting fluorescence corresponding to the $D_1 \rightarrow D_0$ transition. Thus, the vibronic spectra observed with CESE scheme is similar to the dispersed fluorescence (DF) spectra obtained by exciting the origin band of the electronic transition, in which the spacing of the vibronic bands from the origin band represents the vibrational mode frequencies in the ground electronic state, as shown in Figure 1.

In chlorobenzyl radicals, the electronic interaction between the Cl atom and the aromatic ring is undoubtedly of the second-order compared to the interaction between the methylene group and the ring, since the molecule has a planar structure with 7 delocalized π electrons. Thus, the 2,6-dichlorobenzyl radical should exhibit a close relation to those of the benzyl radical of 7 delocalized π electrons, and one might be able to relate the two lowest lying electronic states of the 2,6-dichlorobenzyl radical to the parent benzyl $2^2B_2(D_2)$ and $1^2A_2(D_1)$ states.[20]

The monochromator was scanned at the step of 1.0 cm^{-1} over 1 hour with a slit openness of 0.1 mm from 18000 to

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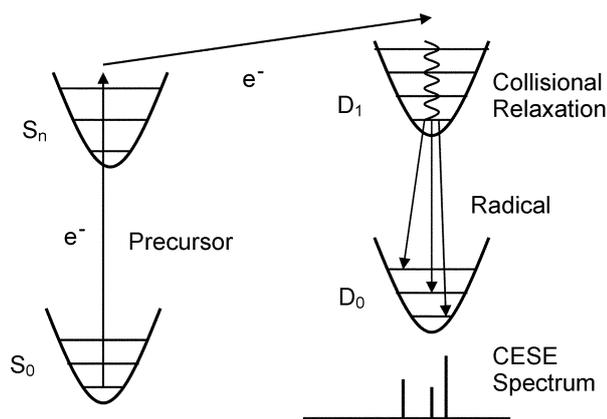
Figure 1. Scheme of CESE spectroscopy for observation of the vibronic emission spectrum of the jet-cooled 2,6-dichlorobenzyl radical.
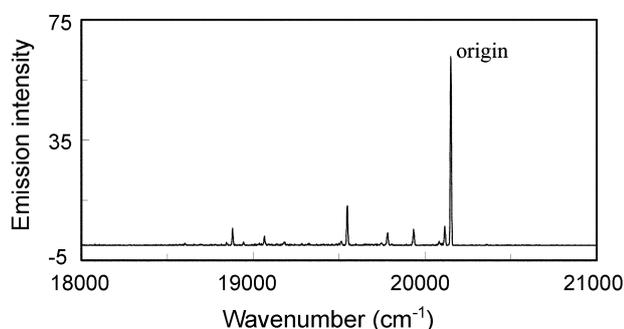
Figure 2. A portion of vibronic emission spectrum of the jet-cooled 2,6-dichlorobenzyl radical in the $D_1 \rightarrow D_0$ transition which has been generated from 2,6-dichlorotoluene with a carrier gas He in a corona excited supersonic expansion.

Table 1. Position of origin band of benzyl-type radicals

Molecules	Isomers	Position (cm^{-1})
methyl-substitution[a]	ortho-	21345
	meta-	21485
	para-	21700
	2,6-dimethyl-	21164
fluorine-substitution[b]	ortho-	21924
	meta-	21691
	para-	21527
	2,6-difluoro-	21774
chlorine-substitution[c]	ortho-	21040
	meta-	21194
	para-	21645
	2,6-dichloro-[d]	20153

[a]References 4-6 and 10. [b]References 7-9 and 11. [c]References 22-24. [d]This work.

$D_1 \rightarrow D_0$ transition was identified with excellent S/N from the vibronic emission spectrum and compared with that of the other benzyl-type radicals, which might be useful for the spectroscopic analysis of benzyl-type radicals.

22000 cm^{-1} to obtained the vibronic emission spectrum shown in Figure 2 of the 2,6-dichlorobenzyl radical in the $D_1 \rightarrow D_0$ transition. The wavenumber of the spectrum was calibrated using the He atomic lines[21] observed at the same spectral region as the 2,6-dichlorobenzyl radical, and is believed to be accurate within $\pm$ 0.5 cm^{-1}.

The strongest band at 20153 cm^{-1} was tentatively assigned to the origin band of the 2,6-dichlorobenzyl radical in the $D_1 \rightarrow D_0$ transition, since no band of noticeable intensity existed to the blue of the origin band. The position of the origin bands were compared with other benzyl-type radicals in Table 1. The origin bands of *o*-, *m*-, and *p*-fluorobenzyl radicals[7-9] are observed at 21924, 21691, and 21527 cm^{-1}, respectively, while that of the 2,6-difluorobenzyl radical[11] at 21774 cm^{-1}. However, the chlorobenzyl radicals[22-24] showed an inverse trend in the position of the origin band, in which the *o*-, *m*-, and *p*-chlorobenzyl radicals had the origin band at 21040, 21194, and 21645 cm^{-1}, respectively

In summary, the jet-cooled 2,6-dichlorobenzyl radical was formed in a corona-excited supersonic expansion using a pinhole-type glass nozzle from 2,6-dichlorotoluene seeded in a large amount of carrier gas He. The origin band of the

References and Notes

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