

Observation of Vibronic Emission Spectra of Jet-Cooled *o*-Chlorobenzyl Radical

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Since benzyl-type radicals are one of the most important species in the chemical reactions of aromatic compounds, their electronic structure has been the subject of many spectroscopic works.¹⁻³ The weak visible fluorescence is believed to arise from the transitions from the close-lying excited electronic D₂ and D₁ states to the ground D₀ state, in which two excited electronic states are mixed by vibronic coupling. Also, ring substitution is expected to affect the energies of two excited electronic states differently as well as vibrational mode frequencies.

Among mono-substituted benzyl radicals, the fluorine substituted radicals have been well examined due to the strong emission intensity.³ The highly symmetric *p*-fluorobenzyl radical has been extensively studied by many experimental techniques.³⁻⁶ Many of the vibrational modes have been assigned by the LIF-DF spectra⁴ and theoretical calculations. Recently, the vibronic emission spectra of *meta*-⁷ and *ortho*-isomers⁸ have been observed by the technique of corona excited supersonic expansion.

Although chlorine substituted benzyl radicals are believed to be important intermediates in the combustion process of chemicals containing chlorine atom, the spectroscopic studies are limited due to the weak intensity of fluorescence in the visible region. It has been well known that the fluorescence intensity of aromatic compounds quickly decreases with the increasing mass of substituents on the aromatic ring. Of three chlorobenzyl radical isomers, the *p*-chlorobenzyl radical has been observed in the liquid phase⁹ as well as in the gas phase,^{10,11} in which several vibrational modes were assigned from the vibronic emission spectrum. Recently, Lee and Chae¹² have succeeded in observing the vibronic emission spectrum of the *m*-chlorobenzyl radical generated in a corona excited supersonic expansion (CESE) and assigned several vibrational modes in the ground electronic state. To date, however, no one has reported any spectroscopic data for *o*-chlorobenzyl radical in any spectral range.

In this work, we report, for the first time, the observation of the visible vibronic emission spectrum of the jet-cooled *o*-chlorobenzyl radical generated from *o*-chlorotoluene seeded in a large amount of inert carrier gas He using a pinhole-type glass nozzle in a CESE, in order to elucidate the spectroscopic identification on the chlorobenzyl radicals.

The *o*-chlorobenzyl radical was produced in a jet from *o*-chlorotoluene and vibronically excited with a large amount of carrier gas He in a CESE which has been described elsewhere.¹³ Reagent grade *o*-chlorotoluene, which was purchased from the Aldrich and used without further purification, was vaporized in a He atmosphere at room temperature under 2.0 atm of pressure. The concentration of precursor in the carrier gas was adjusted to minimize the emission of He atomic lines and believed to be about 1% in the gas mixture.

The *o*-chlorotoluene was expanded with the carrier gas He through the 0.3 mm diameter of pinhole-type glass nozzle made in this laboratory according to the method described previously.¹⁴ The sharpened long tungsten wire acting as an anode was connected to the high voltage dc power supply, in which the axial discharging current was 5 mA at 1500 V dc potential and stabilized using a 150 kΩ current limiting ballast resistor.

The Pyrex expansion chamber of six-way cross type was made of thick walled Pyrex tubes (Chemglass CG-138-02) of 50 mm in diameter. The chamber was evacuated by two 800 L/min mechanical vacuum pumps, resulting in a pressure range of 0.5-1.0 Torr during continuous expansion with 2.0 atm of backing pressure. The cathode, made of a long copper rod, was positioned to be in parallel with the jet direction under the expansion chamber to avoid arching noise reaching the spectrometer.

It has been known that the well-controlled corona discharge of substituted toluenes with a large amount of inert buffer gases predominantly produce corresponding benzyl-type radicals in the excited electronic state. The blue-green color was evidence for the presence of the *o*-chlorobenzyl radical in the jet. The spectral region from 18000 to 24000 cm⁻¹ was scanned at increments of 0.5 cm⁻¹ over 2 hr to obtain the final spectrum shown in Figure 1. The wavenumber of the spectrum was calibrated using the He atomic lines¹⁵ observed at the same spectral region as the *o*-chlorobenzyl radical and is believed to be accurate within ± 0.5 cm⁻¹.

The similarity of electronic structure between *o*-chlorobenzyl and benzyl radicals confirms that the chlorine atom makes insignificant contribution to the electronic density of benzene ring. Thus, the *o*-chlorobenzyl radical should exhibit a close relation to that of the benzyl radical and one may be able to relate the two lowest lying electronic states of *o*-chlorobenzyl to parental benzyl 2²B₂(D₂) and 1²A₂(D₁)

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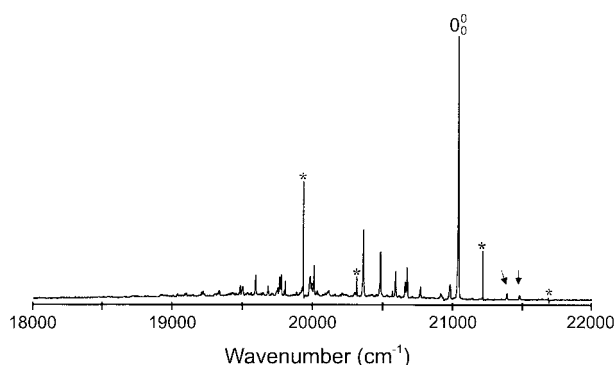


Figure 1. A portion of visible vibronic emission spectrum of the jet-cooled *o*-chlorobenzyl radical in the $D_1 \rightarrow D_0$ transition. The peaks marked with an asterisk and arrow in the spectrum indicate He atomic lines and the bands from benzyl radical, respectively.

states, in which the $1^2A_2(D_1)$ state is the lowest excited electronic state like the benzyl radical.¹⁶

Figure 1 shows a portion of the visible vibronic emission spectrum of the *o*-chlorobenzyl radical in the $D_1 \rightarrow D_0$ transition. Most of the strong bands are observed with an excellent S/N in the region of 19000–21500 cm^{-1} . It consists of a strong origin band of the $D_1 \rightarrow D_0$ transition at 21040.0 cm^{-1} (in air), followed to lower energies by a series of vibronic bands. Several well-resolved strong bands observed at 20674.2, 20592.5, 20483.6, 20362.4, and 20013.6 cm^{-1} are tentatively assigned as the transitions of $9b_1^0$, $7a_1^0$, $6b_1^0$, $6a_1^0$, and 1_1^0 , respectively, by comparing with those of *o*-chlorotoluene. However, the more reasonable assignment could be obtained from *ab initio* calculations using the GAUSSIAN 98 program.

The absence of bands with observable intensity to the blue of the origin clearly confirms the efficient vibrational cooling at the excited electronic state, which is an important characteristic of the pinhole-type glass nozzle in a CESE. The transition from the D_2 state has not been observed in the spectra possibly due to the collisional relaxation of electronic energy through vibronic coupling between the electronic excited D_2 and D_1 states as shown in Figure 2. The absence of transition from the D_2 state was identified from the vibronic emission spectra of many benzyl-type radicals except for the *p*-chlorobenzyl radical in which the vibronic coupling is very weak since the D_2 state is only 94 cm^{-1} above the D_1 state. The weak but clear bands at 21480.5 and 21390.1 cm^{-1} are from the $6a_1^0$ and $6b_1^0$ transitions of benzyl radical, respectively, which generated from the impurities in the sample. The trace amount of toluene was also identified in the gas chromatographic method. By taking the vacuum correction into account, the measured band frequencies of benzyl radical agree well with those reported previously.²

The vibrational structure of the *o*-chlorobenzyl radical appears in the region of 200–2000 cm^{-1} from the origin band, which does not continue as far as *o*-chlorotoluene. The strongest intensity of the origin band indicates that the molecule at both the ground and the excited electronic states has a planar structure with a similar geometry.

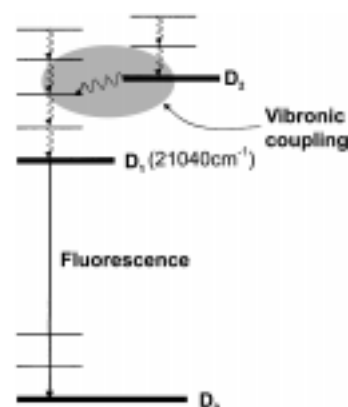


Figure 2. The scheme of the vibronic transition of the *o*-chlorobenzyl radical with the path of collisional relaxation prior to the radiative transition.

Since the spectra observed with a pinhole-type glass nozzle are similar to the LIF-DF spectra obtained by exciting the origin band of the electronic transition, the spacing of the vibronic bands from the origin band represents the vibrational mode frequencies at the ground state. The assignments of the vibrational modes could be made from an *ab initio* calculation and the mode analysis.

In summary, the *o*-chlorobenzyl radical was generated in the jet from *o*-chlorotoluene with a large amount of carrier gas He and vibronically excited in a CESE using a pinhole-type glass nozzle. The vibronic emission spectrum of the *o*-chlorobenzyl radical in the $D_1 \rightarrow D_0$ transition was recorded, for the first time, using a long path double monochromator in the visible region, from which the lowest excited electronic state is found to locate 21040 cm^{-1} above the ground state.

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References

- Cossart-Magos, C.; Leach, S. *J. Chem. Phys.* **1976**, *64*, 4006.
- Selco, J. I.; Carrick, P. G. *J. Mol. Spectrosc.* **1989**, *137*, 13.
- Cossart-Magos, C.; Cossart, D. *Mol. Phys.* **1988**, *65*, 627.
- Suh, M. H.; Lee, S. K.; Miller, T. A. *J. Mol. Spectrosc.* **1999**, *194*, 211.
- Lee, S. K.; Baek, D. Y. *Chem. Phys. Lett.* **1999**, *301*, 407.
- Fukushima, M.; Obi, K. *J. Chem. Phys.* **1990**, *93*, 8488.
- Lee, S. K.; Ahn, B. U. *Chem. Phys. Lett.* **2000**, *321*, 25.
- Lee, S. K.; Lee, S. K. *J. Phys. Chem. A* **2001**, *105*, 3034.
- Tokumura, K.; Udagawa, M.; Ozaki, T.; Itoh, M. *Chem. Phys. Lett.* **1987**, *141*, 558.
- Fukushima, M.; Obi, K. *Chem. Phys. Lett.* **1996**, *248*, 269.
- Lee, S. K.; Baek, D. Y. *Chem. Phys. Lett.* **1999**, *304*, 39.
- Lee, S. K.; Chae, S. Y. *J. Phys. Chem. A* **2001**, *105*, 5808.
- Han, M. S.; Choi, I. S.; Lee, S. K. *Bull. Korean Chem. Soc.* **1996**, *17*, 991.
- Lee, S. K. *Bull. Korean Chem. Soc.* **1998**, *19*, 145.
- Wiese, M. L.; Smith, M. W.; Glennon, B. M. *Atomic Transition Probabilities*; NSRD-NBS4: 1966.
- Hiratsuka, H.; Mori, K.; Shizuka, H.; Fukushima, M.; Obi, K. *Chem. Phys. Lett.* **1989**, *157*, 35.