Vibronic Emission Spectroscopy of the Jet-Cooled *o*-Chlorobenzyl Radical in the $D_1 \rightarrow D_0$ Transition

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The jet-cooled *o*-chlorobenzyl radical has been generated for the first time from *o*-chlorotoluene seeded in a large amount of inert carrier gas He and vibronically excited using a pinhole-type glass nozzle in a corona excited supersonic expansion. The vibronic emission spectrum of the *o*-chlorobenzyl radical in the $D_1 \rightarrow D_0$ transition has been recorded with a long path monochromator in the visible region. The spectrum has been analyzed to determine accurate electronic transition and vibrational mode frequencies in the ground electronic state by comparison with those from an ab initio calculation as well as those of *o*-chlorotoluene.

Introduction

The assignments of vibrational modes of large aromatic radicals are of interest for identification of molecular species generated in the combustion process.[1,2] However, the spectroscopic information on transient species in the gas phase is limited when there is a large number of vibrational modes and difficulty in the production of the species in concentrations high enough to be detected. Nevertheless, Jacox[3] has recently tabulated the spectroscopic data of many transient species.

The supersonic free jet expansion has been proven to be a very useful spectroscopic technique for molecular species in the gas phase.[4,5] The spectral simplification and stabilization associated with the expansion of inert carrier gas cannot be obtained in any other way. The combination of the supersonic expansion technique with emission spectroscopy has had an enormous impact on the repertoire of spectroscopic studies of molecular species that cannot be carried out. Of the emission sources developed so far for these purposes, the only one giving enough continuous photon intensity for high-resolution studies of weak transition is the Engelking-type nozzle,[6,7] which has been widely employed for the observation of vibronic emission spectra of transient molecules. This has been also applied to the observation of vibronic emission spectra of jet-cooled benzyl-type radicals in the gas phase.[8−19]

Among many benzyl-type radicals, the chlorine-substituted benzyl radicals have been less studied in comparison with the fluorine-substituted benzyl radicals due to the weak emission intensity. 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 the chlorobenzyl radicals, the *p*-isomer has been examined by a few spectroscopic techniques. The energy levels and symmetry of the excited electronic state have been investigated in the liquid phase.[21] Several vibrational modes in the ground electronic state of the *p*-isomer have been accurately identified by applying the laser-induced fluorescence technique[20] and the corona-excited supersonic expansion technique.[12] Recently, Lee's group[19] has generated *m*-chlorobenzyl radicals and assigned vibrational modes to the *m*-chlorobenzyl radical in the ground electronic state from the vibronic emission spectrum. To date, however, no one has reported any spectroscopic data for *o*-chlorobenzyl radicals.

In this work, we report, for the first time, the vibronic emission spectrum of the jet-cooled *o*-chlorobenzyl radical in the $D_1 \rightarrow D_0$ transition, from which the vibrational modes have been assigned in the ground electronic state by comparison with those from an ab initio calculation and *o*-chlorotoluene. The results will elucidate the spectroscopic identification of chlorobenzyl radical isomers in the combustion process together with those reported for *m*- and *p*-isomers.

Experimental Section

The experimental setup employed in this work is similar to those described elsewhere.[22,23] The generation and excitation of the *o*-chlorobenzyl radical have been carried out in a corona excited supersonic expansion (CESE). Briefly, it consisted of a pinhole-type glass nozzle coupled with a high voltage power supply, a Pyrex expansion chamber, and a spectrometer for the observation of vibronic emission spectrum.

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. Reagent grade *o*-chlorotoluene, which was purchased from Aldrich and used without further purification, was vaporized in a He atmosphere at room temperature under 2.0 atm pressure. The experimental conditions have been adjusted to obtain the maximum intensity of fluorescence monitored from the origin band of the transition, which shows the strongest intensity in the emission spectrum. 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 0.4 mm diameter pinhole-type glass nozzle made in this laboratory according to the method described previously.[23] 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 resister.

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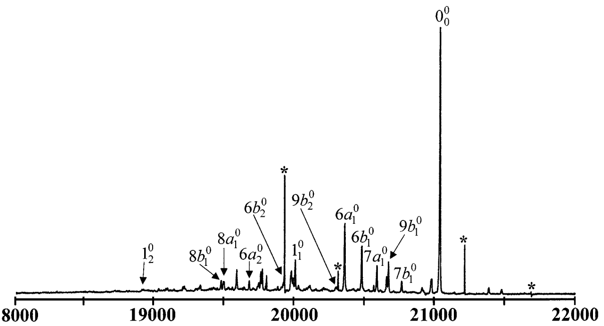

Figure 1. Portion of the vibronic emission spectrum of the jet cooled *o*-chlorobenzyl radical in the $D_1 \rightarrow D_0$ transition in units of wavenumber. The peaks marked with an asterisk in the spectrum indicate the He atomic transitions.

In the original nozzle developed by Engelking,[7] the coronal electrode sits just behind the nozzle opening on the high-pressure side, which leads to excitation before expansion, causing the problem of nozzle clogging when heavy organic compounds were employed as a precursor. Thus, we have made the metal tip of the anode extend through the nozzle to reduce clogging of the nozzle throat by decomposition products and soot deposits of *o*-chlorotoluene. Although the metal tip was exposed less than 1.0 mm outside the end of the nozzle capillary, this significantly reduced the clogging problem by partially allowing excitation to occur after expansion. The modified pinhole type nozzle has been applied to many benzyl-type radicals.[11−13,15−19]

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 in parallel with the jet direction under the expansion chamber to avoid arching noise reaching the spectrometer.

A weak blue-green colored jet was evidence for the presence of the *o*-chlorobenzyl radicals in the expansion. The visible radiation emanating from the downstream jet area 5 mm away from the nozzle opening was collimated by a quartz lens ($f = 5.0$ cm) placed inside the expansion chamber and focused onto the slit of the monochromator (Jobin Yvon U1000) containing two 1800 lines/mm gratings, and detected with a cooled photomultiplier tube (Hamamatsu R649) and a photon counting system. During the scans, the slits were set to 0.100 mm, providing an effective resolution of about 1 cm^{-1} at the visible region. The spectral region from 18 000 to 24 000 cm^{-1} was scanned at increments of 0.5 cm^{-1} over 2 h to obtain the final spectrum shown in Figure 1. The wavenumber of the spectrum was calibrated using He atomic lines[24] observed at the same spectral region as the *o*-chlorobenzyl radical and is believed to be accurate within ± 0.5 cm^{-1}.

Because the *o*-chlorobenzyl radical has many vibrational modes and the assignments have not been completed, ab initio calculations on the D_0 state have been carried out to assist the assignment of the vibronic structure of the spectrum. The calculations were executed with a personal computer equipped with an Intel Pentium 600 MHz processor and 128 MB RAM, and with the standard methods included in the GAUSSIAN 98 program for Windows. The geometry optimization and vibrational frequency calculations were carried out at the UHF level and the 6-31 g* basis set was employed in all calculations.

Results and Discussion

It has been known in a CESE that the well-controlled corona discharge of substituted toluenes with a large amount of inert buffer gases predominantly produces corresponding benzyl-type radicals in the excited electronic state. Also, the weak visible emission from benzyl-type radicals is believed to arise from transitions to the 1^2B_2 ground state from the close-lying 2^2B_2 and 1^2A_2 excited electronic states whose energies are affected differently by ring substitution. The predicted closeness of the first two excited electronic states of benzyl-type radicals makes it particularly interesting to examine perturbation effects on the electronic structure and spectra.[25] In the *o*-chlorobenzyl radical, the electronic interaction between the aromatic ring and the chlorine atom is undoubtedly of second-order compared to the interaction between the methylene group and the ring because the molecule has a planar structure with seven delocalized π electrons. The similarity of electronic energy levels between *o*-chlorobenzyl and benzyl-type radicals confirms that the chlorine atom makes an insignificant contribution to the electronic density of the 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 $2^2B_2(D_2)$ and $1^2A_2(D_1)$ states, in which the 1^2A_2 state is the lowest excited electronic state like the benzyl radical.

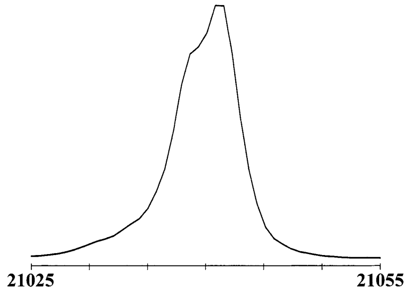

Figure 2. Band shape of the origin band of the *o*-chlorobenzyl radical in the $D_1 \rightarrow D_0$ transition in units of wavenumber, which shows the doublet partially separated by 2.4 cm^{-1}.

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 19 000−21 500 cm^{-1}. It consists of a strong origin band of the $D_1 \rightarrow D_0$ transition at 21 040.0 cm^{-1} (in air), followed to lower energies by a series of vibronic bands. Because most of the strong bands show band shapes of doublet in the spectrum, as shown in Figure 2, partially separated by an average of 2.4 cm^{-1}, the frequency of each band was measured at the minimum intensity between the doublet.

The observation of other types of isomers in a corona discharge has been discussed in detail by Selco and Carrick for the xylyl radicals.[9] Although the mechanism of excitation is not exactly known for the CESE source, there is clearly enough energy available to break an α-hydrogen and still leave the resulting radical with electronic excitation energy. During the excitation and bond-breaking process of *m*-xylene, the radical may be excited through a prismane- or benzvalence-type intermediate, which results in the appearance of the *o*- and *p*-xylyl radicals in the spectra of the *m*-xylyl radical.

The absence of bands with observable intensity to the blue of the origin band clearly confirms the efficient vibrational cooling at the excited electronic state, which is an important characteristic of the pinhole-type glass nozzle. The weak but clear bands at 21 480.5 and 21 390.1 cm^{-1} are from the $6a_1^0$ and $6b_1^0$ transitions of the benzyl radical,[8] respectively, which is generated from the impurities in the sample. By taking the vacuum correction into account, the measured band frequencies of the benzyl radical agree well with those reported previously.[8] The trace amount of toluene has been identified by the analytical method.

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. Most of the modes that are active in the *o*-chlorobenzyl radical are the in-plane ring deformation modes that are not in the parent molecule. This indicates that there is either interaction between the unpaired electron and the benzene ring electrons or that the *o*-chlorobenzyl radical in the D_1 state has a planar structure.

Because the spectra observed with a pinhole-type glass nozzle are similar to the dispersed fluorescence 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 electronic state.[26,27]

The observed vibronic bands were assigned by comparison with the known vibrational frequencies of *o*-chlorotoluene[28,29] as well as those from an ab initio calculation. From the comparison, it seems clear that the vibrational structures in the ground electronic state of both molecules are subjected to the isodynamic approximation that describes the correspondence of vibrational mode frequencies and transition intensity between the molecules with similar structure. This has been applied to the vibronic assignments of many benzyl-type radicals. The bands observed in this work are listed in Table 1, together with their assignments.

For the direct application of isodynamic approximations, which are applied to the fluorobenzyl radicals, we have also tried to obtain the emission spectrum of *o*-chlorotoluene in the $S_1 \rightarrow S_0$ transition under similar experimental conditions in the UV region, but could only observe the $A^2\Delta \rightarrow X^2\Pi$ transition of C−Cl,[30] which is one of the main decomposition fragments of the precursor. Thus, the vibrational mode frequencies given by Varsanyi[28] and by Ichimura et al.[31] have been cited in this work. From the comparison with those of *o*-chlorotoluene, it seems clear that the vibrational structures of both molecules are well subjected to the isodynamic approximation. Thus, most of the bands observed were assigned by comparison with the vibrational mode frequencies of *o*-chlorotoluene as well as an ab initio calculation.

In the *p*-chlorobenzyl radical, the vibrational mode symmetry has been determined from the band shapes because the transition dipole moment is parallel to the "a" or "b" inertial axis for in-plane vibrations. However, the band shape cannot be easily distinguished for the *m*- and *o*-isomers because the transition dipole moment has a hybrid type. The rotational contour analysis of the origin band of the *o*-xylyl radical shows that the dipole moment is oriented at +37° or −37° with respect to the "b" inertial axis.[32] For the *o*-chlorobenzyl radical, which belongs to the C_s point group, the vibrational modes have the a′ and a″ symmetry for in-plane and out-of-plane vibrations, respectively.

It has been generally accepted that the calculation using GAUSSIAN 98 at the UHF level with a 6-31 g* basis set predicts the vibrational mode frequencies within ±10% from the experimental values. The calculation has been carried out as described in the Experimental Section. From the calculation for the *o*-chlorobenzyl radical, a total of 36 vibrational mode frequencies have been obtained, of which 25 and 11 vibrational modes belong to the a′ and a″ symmetry in the C_s point group, respectively. The calculated values have been multiplied by a scaling factor of 0.940 to correlate with the observed values, as in the case of *m*- and *p*-chlorobenzyl radicals. Table 2 lists the observed and calculated vibrational mode frequencies of the *o*-chlorobenzyl radical as well as those of the *o*-chlorotoluene[28] with the symmetry of vibrational modes.

TABLE 1: List of the Vibronic Bands Observed and Their Assignments[a]

position	intensity[b]	spacing fromorigin	assignments
21480.50	2	(440.50)	benzyl(6a)
21390.10	2	(350.10)	benzyl(6b)
21217.08	18	(177.08)	He atomic line
21040.00	100	0.00	origin (0_0^0)
20981.80	6	58.20	+58.20
20914.40	2	125.60	$10b_1^0$
20794.60	1	245.40	$10a_1^0$
20770.00	5	270.00	$7b_1^0$
20711.30	1	328.70	+58.70
20674.20	12	365.80	$9b_1^0$
20661.00	7	379.00	$16b_1^0$
20616.00	2	424.00	+58.20
20592.50	11	447.50	$7a_1^0$
20570.30	3	469.70	$16a_1^0$
20534.20	2	505.80	+58.30
20483.60	18	556.40	$6b_1^0$
20456.70	1	583.30	benzyl(8b)
20425.90	2	614.10	+57.70
20362.40	26	677.60	$6a_1^0$
20316.90	8	723.10	He atomic line
20310.20	4	729.80	$9b_2^0$
20304.30	3	735.70	+58.10
20300.00	3	740.00	11_1^0
20226.90	2	813.10	$7a_1^0\ 9b_1^0$
20212.50	2	827.50	$7b_1^0\ 6b_1^0$
20117.40	3	922.60	$9b_1^0\ 6b_1^0$
20107.90	3	932.10	$17b_1^0$
20092.60	2	947.40	$6a_1^0\ 7b_1^0$
20076.30	2	963.70	5_1^0
20036.50	3	1003.50	$7a_1^0\ 6b_1^0$
20013.60	13	1026.40	1_1^0
19997.60	6	1042.40	$6a_1^0\ 9b_1^0$
19986.00	9	1054.00	$18a_1^0$
19982.50	8	1057.50	$17b_1^0\ 10b_1^0$
19955.40	2	1084.60	+58.20
19937.20	44	1102.80	He atomic line
19934.80	6	1105.20	$9b_1^0\ 11_1^0$
19928.00	6	1112.00	$6b_1^0$
19914.80	3	1125.20	$6a_1^0\ 7a_1^0$
19889.40	3	1150.60	$9a_1^0$
19810.50	7	1229.50	He atomic line
19806.20	4	1233.80	$6a_1^0\ 6b_1^0$
19779.30	9	1260.70	14_1^0
19768.80	8	1271.20	$1_1^0\ 10a_1^0$
19753.80	4	1286.20	$9b_1^0\ 6b_1^0$
19685.20	5	1354.80	$6a_2^0$
19648.00	3	1392.00	$1_1^0\ 9b_1^0$
19622.00	2	1418.00	$6a_1^0\ 11_1^0$
19595.40	9	1444.60	$19a_1^0$
19565.10	3	1474.90	$19b_1^0$
19551.40	2	1488.60	$6b_1^0\ 17b_1^0$
19500.10	5	1539.90	$8a_1^0$
19484.30	5	1555.70	$8b_1^0$
19336.50	3	1703.50	$5_1^0 11_1^0$
19223.80	3	1816.20	$6b_1^0\ 14_1^0$
19213.80	3	1826.20	$7b_1^0\ 8b_1^0$
18932.60	2	2107.40	$18a_2^0$

[a] Measured in air (cm^{-1}). [b] Normalized with respect to the strongest band.

The radial skeletal vibrational mode 1 of a benzene ring breathing was assigned to the fairly strong band at 1026.4 cm^{-1} because the frequency of this mode should coincide with that of *o*-chlorotoluene (1054 cm^{-1}). The calculation (1021.4 cm^{-1})

TABLE 2: Vibrational Mode Frequencies (cm^{-1}) of the *o*-Chlorobenzyl Radical[a]

mode[b]	this work (D$_0$)	ab initio[c] UHF/6-31G* (D$_0$)	*o*-chlorotoluene[d] (S$_0$)	symmetry (C_s)
origin	21040.00			
10b	125.60	131.39	164	a″
10a	245.40	233.00	246	a″
7b	270.00	270.69	160−265	a′
9b	365.80	373.18	366	a′
16b	379.00	400.45	437	a″
7a	447.50	449.67	445	a′
16a	469.70	473.67	508	a″
6b	556.40	552.88	553	a′
6a	677.60	666.10	678	a′
11	740.00	741.74	750	a″
17b	932.10	916.29	935	a″
5	963.70	950.54	970	a″
1	1026.40	1010.66	1054	a′
18a	1054.00	1063.30	1126	a′
9a	1150.60	1127.62	1155	a′
14	1260.70	1248.02	1279	a′
19a	1444.60	1456.85	1458	a′
19b	1474.90	1465.15	1473	a′
8a	1539.90	1529.64	1572	a′
8b	1555.70	1546.00	1589	a′

[a] Measured in air (cm^{-1}). [b] Reference 33. [c] Multiplied by a scaling factor of 0.940. [d] Reference 28.

TABLE 3: Anharmonicities of Normal Modes of the *o*-Chlorobenzyl Radical[a]

mode[b]	ω_e	$\omega_e\chi_e$
6a	678.0	0.2
6b	557.2	0.4
18a	1054.6	0.3

[a] In units of cm^{-1}. [b] Reference 33.

agrees well with the observation. The very strong well-resolved bands at 677.6 and 556.4 cm^{-1} were assigned to modes 6a and 6b of C−C−C angle deformation, respectively, which are degenerate at about 606 cm^{-1} in benzene. The splitting between 6a and 6b increases with the increasing mass of the substituents of the benzene ring. The splitting is only 59 cm^{-1} for *o*-fluorobenzyl, but it increases to 121 cm^{-1} for *o*-chlorobenzyl. With splitting, mode 6b has a higher frequency than mode 6a for the *p*-isomer, but the trend is reversed for the *o*- and *m*-isomers. The observations are in excellent agreement with the calculations (673.2 and 558.8 cm^{-1}). The bands with strong intensities at 447.5 and 365.8 cm^{-1} were assigned to mode 7a of the C−Cl stretching and mode 9b of the C−Cl in-plane bending vibrations, respectively, which form a strongly coupled pair and show diminishing frequency upon substitution of the benzene ring. Both modes are in accord with the calculation (454.5 and 377.2 cm^{-1}) as well as the precursor (445 and 366 cm^{-1}). Mode 7a was strongly observed from the *p*-isomer at the analogous frequencies. Mode 9b also shows strong intensity in the vibronic emission spectrum of *o*-fluorobenzyl. Another coupled pair of modes 7b and 9a was observed with weak intensities at 270.0 and 1150.6 cm^{-1}, respectively, and the calculation (273.6 and 1139.6 cm^{-1}) agrees well with the observation. The degenerate mode 8 of the C−C stretching vibration is split by substitution into modes 8a and 8b. In the *p*-isomer, the frequency of the mode 8a component is higher than that of mode 8b, whereas in the *m*- and *o*-isomers, the case is reversed. The bands with medium intensities at 1539.9 and 1555.7 cm^{-1} were assigned to modes 8a and 8b, respectively. The observation agrees well with not only the calculation (1545.9 and 1562.5 cm^{-1}) but also the precursor (1572 and 1589 cm^{-1}). Although heavy halogen atoms undoubtedly cause frequency diminution, other C−C stretching modes (19a and 19b), which are not very sensitive to substitution, were observed with reasonable intensity. The bands at 1444.6 and 1474.9 cm^{-1} were assigned to modes 19a and 19b, respectively. Both the calculation (1472.4 and 1480.7 cm^{-1}) and the precursor (1458 and 1473 cm^{-1}) are consistent with the observation. The frequency of component 19a is lower than that of 19b as the frequency 8a is related to 8b. Another strong band at 1054 cm^{-1} was assigned to the 18b mode of the C−Cl in-plane bending vibration due to the agreement with the calculation (1074.6 cm^{-1}). Finally, the 14 mode of the C−C stretching vibration was assigned to the strong band at 1150.6 cm^{-1} because both the calculation and the precursor agree well with the observation. The frequency of mode 14 is not very sensitive to substitution, either. In this work, the modes with a′ symmetry of in-plane vibration were observed with much stronger intensity compared to the out-of-plane modes with a″ symmetry.

For vibrational modes with a″ symmetry, which generally show weak intensity, mode 16b of the out-of-plane skeletal vibration was observed with fairly strong intensity at 379.0 cm^{-1} whereas the very weak band at 469.7 cm^{-1} was assigned to the counterpart mode 16a due to correlation with the calculation as well as the precursor. The frequency of vibrational component 16 rises with substitution as a result of coupling with out-of-plane C−Cl vibrations of lower frequencies. A similar tendency was also observed from *o*-fluorobenzyl. Mode 5 of the C−H out-of-plane vibration was assigned to the well-resolved band at 963.7 cm^{-1} because it has an excellent agreement with the calculation (960.7 cm^{-1}), which has the highest frequency with a″ symmetry. Modes 10a and 10b of the C−H out-of-plane vibration were assigned to the very weak but well-resolved bands at 245.4 and 125.6 cm^{-1}, respectively, in which both show very good correlation with the calculation (235.5 and 132.8 cm^{-1}). The calculated values are the only ones with a″ symmetry in the range 160−410 cm^{-1}. Finally, other weak bands at 740.0 and 932.1 cm^{-1} were assigned to modes 11 and 17b, respectively, because the calculation predicts excellent agreement.

Relatively short progressions involving the vibrational modes 9b (365.8 cm^{-1}), 6b (556.4 cm^{-1}), 6a (677.6 cm^{-1}), and 18a (1054.0 cm^{-1}) were identified. From the measurement of band position of the overtone bands, we could determine the vibrational harmonic frequency and anharmonicity that are listed in Table 3. The values determined in this work are similar to those reported for the xylyl radicals.[9] The vibrational modes with the strong intensity listed above are also active in combination bands, in which the modes with the same symmetry combine.

As described above, we have not observed any band belonging to the *o*-chlorobenzyl radical in the blue region of the origin band in the spectrum. Instead, a sequence band has been regularly observed in the vicinity of every strong vibronic band at the interval of approximately −58 cm^{-1} from the vibronic band.

A problem remains in explaining the origin of the low-frequency sequence band. Cossart-Magos and Cossart[32] have observed several weak bands near the origin band of the *p*-fluorobenzyl radical and assigned them as combination bands coupled with the origin band. Fukushima and Obi have observed several bands in the vicinity of the strong bands and attributed them as belonging to the van der Waals molecules.[26] However, it seems unlikely in this study that the band could be attributed to dimers or van der Waals molecules because the same bands were observed with Ar carrier gas, which gives a much poorer S/N for the spectrum. Another possibility might be that the band is due to impurities in the sample because the sample contains less than 1% of isomers. However, we could not even detect the origin bands of the *m*- and *p*-chlorobenzyl radicals[19,12] in the spectrum at the positions reported previously. Thus, it does not seem likely that this is a possible explanation for the sequence band.

A possible explanation of the low-frequency sequence band might be attributed to the sequence band associated with the most intensive bands in the spectrum because the intensity of the sequence band is proportional to that of the strong vibronic bands. Although Cossart-Magos and Cossart[32] have assigned the $16a^0_1 11^0_1$, $18b^1_1$, 11^1_1, and $10b^1_1$ for the bands observed at -11.3, $+7.1$, -27.2, and -54.8 cm^{-1}, respectively, from the origin band of *p*-fluorobenzyl radical in the $D_1 \rightarrow D_0$ transition, it may not be possible at this moment to attempt the assignment of the band due to the insufficient vibrational mode frequencies at the excited electronic state.

In summary, the *o*-chlorobenzyl radical was generated in the jet from the *o*-chlorotoluene with a large amount of carrier gas He and vibronically excited in the corona-excited supersonic expansion using a modified Engelking type nozzle. The vibronic emission spectrum of the *o*-chlorobenzyl radical in the $D_1 \rightarrow D_0$ transition was recorded using a long path double monochromator in the visible region. The spectrum was analyzed to obtain the vibrational mode frequencies at the ground electronic state.

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References and Notes

(1) Eckbreth, A. C.; Bonczyk, P. A.; Verdieck; J. F. Combustion Diagnostics by Laser Raman and Fluorescence Techniques. *Prog. Energy Combust. Sci.* **1979**, *5*, 253−322.

(2) Eckbreth; A. C. *Laser Diagnostics from Combustion Temperature and Species*; Abacus: Tunbridge Wells, U.K., 1988.

(3) Jacox, M. E. Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules. *Journal o Physical and Chemical Reference Data*, Monograph #3; American Chemical Society: Washington, DC, 1994.

(4) Smalley, R. E.; Wharton, L.; Levy, D. H. *J. Chem. Phys.* **1975**, *63*, 4977.

(5) Miller, T. A. *Science* **1984**, *223*, 545.

(6) Droege, A. T.; Engelking, P. C. *Chem. Phys. Lett*. **1983**, *96*, 316.

(7) Engelking, P. C. *Rev. Sci. Instrum*. **1986**, *57*, 2274.

(8) Selco, J. I.; Garrick, P. G. *J. Mol. Spectrosc.* **1989**, *137*, 13.

(9) Selco, J. I.; Garrick, P. G. *J. Mol. Spectrosc.* **1995**, *173*, 277.

(10) Selco, J. I.; Garrick, P. G. *J. Mol. Spectrosc.* **1995**, *173*, 262.

(11) Lee, S. K.; Baek, D. Y. *Chem. Phys. Lett.* **1999**, *301*, 407.

(12) Lee, S. K.; Baek, D. Y. *Chem. Phys. Lett.* **1999**, *304*, 39.

(13) Lee, S. K.; Baek, D. Y. *Chem. Phys. Lett.* **1999**, *311*, 36.

(14) Suh, M. H.; Lee, S. K.; Miller, T. A. *J. Mol. Spectrosc.* **1999**, *194*, 211.

(15) Lee, S. K.; Ahn, B. U. *Chem. Phys. Lett.* **2000**, *320*, 601.

(16) Lee, S. K.; Ahn, B. U. *Chem. Phys. Lett.* **2000**, *321*, 25.

(17) Lee, S. K.; Baek, D. Y. *J. Phys. Chem. A* **2000**, *104*, 5219.

(18) Lee, S. K.; Lee S. K. *J. Phys. Chem. A* **2001**, *105*, 3034.

(19) Lee, S. K.; Chae, S. Y. *J. Phys. Chem. A* **2001**, *105*, 5808.

(20) Fukushima, M.; Obi, K. *Chem. Phys. Lett.* **1996**, *248*, 269.

(21) Tokumura, K.; Udagawa, M.; Ozaki, T.; Itoh, M. *Chem. Phys. Lett.* **1987**, *141*, 558.

(22) Han, M. S.; Choi, I. S.; Lee, S. K. *Bull. Korean Chem. Soc.* **1996**, *17*, 991.

(23) Lee, S. K. *Bull. Korean Chem. Soc.* **1998**, *19*, 145.

(24) Wiese, M. L.; Smith, M. W.; Glennon, B. M. *Atomic Transition Probabilities*; NSRD-NBS4; National Bureau of Standards: Washington , DC, 1966.

(25) Hiratsuka, H.; Mori, K.; Shizuka, H.; Fukushima, M.; Obi, K.*Chem. Phys. Lett.* **1989**, *157*, 35.

(26) Fukushima, M.; Obi, K. *J. Chem. Phys.* **1990**, *93*, 8488.

(27) Suh, M. H.; Lee, S. K.; Rehfuss, B. D.; Miller, T. A.; Bondybey, V. E. *J. Phys. Chem.* **1991**, *95*, 2727.

(28) Varsanyi, G.; *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*; John Wiley & Sons: New York, 1974.

(29) Kojima, H.; Suzuki, T.; Ichimura, T.; Fujii, A.; Ebata, T.; Mikami, N. *J. Photochem. Photobiol. A* **1995**, *92*, 1.

(30) Pearse, R. W. B.; Gatdon, A. G. *The Identification of Molecular Spectra*, 4th ed.; Chapman and Hall: London, 1976.

(31) Ichimura, T.; Kawana, A.; Suzuki, T.; Ebata, T.; Mikami, N. *J. Photochem. Photobiol. A* **1994**, *80*, 145.

(32) Cossart-Magos, C.; Cossart, D. *Mol. Phys.* **1988**, *65*, 627.

(33) Wilson, E. B. *Phys. Rev.* **1934**, *45*, 706.