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Vibrational Mode Assignments of Jet-Cooled *m*-Chlorobenzyl Radical in the Ground Electronic State

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

Introduction

The electronic structure of benzyl-type radicals has been the subject of many spectroscopic works.[1−4] The halogen atom substitution in the benzene ring is believed to affect the electronic structure and vibrational mode frequencies.[5−7] Among monosubstituted benzyl-type radicals, the substitution at para position has been more investigated compared to the other isomers since the symmetry axis does not change from the benzyl radical, thus preserving closely the lineage of the benzyl radical.[5,7−10]

Of the many halogen atom substituted benzyl-type radicals, the fluorine-substituted benzyl radicals have been extensively examined since they emit strong fluorescence in the visible region. In particular, *p*-fluorobenzyl radical was studied by many experimental techniques,[2,5,11,12] and many of the vibrational modes were identified by not only experimental works but also theoretical calculations. Recently, the assignments of vibrational modes of meta-[13] and ortho-isomers[14] have been accomplished using a technique of corona excited supersonic expansion (CESE).

Although chlorine-substituted benzyl-type radicals are believed to be an important intermediate in the combustion process of chemicals containing a chlorine atom, the spectroscopic studies are much limited due to the weak intensity of fluorescence in the visible region. Of the three isomers, the *p*-chlorobenzyl radical has been observed in the liquid phase[15] as well as in the gas phase,[7,16] in which the vibrational modes were assigned from the vibronic emission spectrum. From the analysis of vibrational modes of *p*-chlorobenzyl radical, it has been confirmed that the radical is also well subjected to the isodynamic approximation.[7]

The vibronic emission spectroscopy using an Engelking-type nozzle[17,18] in a corona excited supersonic expansion offers a suitable means for studying the ground electronic state vibrational frequencies of the benzyl-type molecules.[19] The high efficiency of vibrational cooling at the nozzle opening during the expansion provides simple vibronic emission spectra. Thus, this method has been widely used for determining the vibrational mode frequencies and symmetry of large aromatic compounds in the gas phase.[20]

In this work, we report for the first time the observation of the vibronic emission spectra of *m*-chlorobenzyl radical and assignments of the vibrational modes in the ground electronic state by comparison with those of an ab initio calculation as well as from the known vibrational mode frequencies of the precursor.

Experimental Section

The experimental setup employed in this work is similar to those reported elsewhere.[5,23] Briefly, it consists of a pinhole-type glass nozzle coupled with a corona discharge, a Pyrex expansion chamber, and a spectrometer for the vibronic emission spectra.

The jet-cooled *m*-chlorobenzyl radical was generated from *m*-chlorotoluene seeded in He, the carrier gas, is vibronically excited in a corona excited supersonic expansion using a pinhole-type glass nozzle. Reagent-grade *m*-chlorotoluene was vaporized at the ambient temperature under 2.0 atm of carrier gas, in which the concentration of precursor was adjusted for the maximum emission intensity, monitored from the strongest band and believed to be about 1% in the mixture. The gas mixture was expanded through the 0.3 mm diameter of pinhole-type glass nozzle which was made of a thick walled Pyrex glass tube of 12.7 mm outer diameter and 200 mm length and narrowed one end to a capillary by flame heating. The nozzle was terminated abruptly on the vacuum side for the free expansion by grinding the one end until the nozzle opening of the appropriate diameter is formed. The sharpened tungsten rod of 1.5 mm in diameter and 300 mm in length was inserted into the nozzle for the anode and fixed in the center of the pinhole using a couple of Teflon holders.

Since the corona discharge of *m*-chlorotoluene produces soot deposits clogging the nozzle throat, we have employed the modified Engelking-type[19,24] nozzle developed in this laboratory which leads to excitation after expansion. In the original Engelking-type nozzle, the electrode sits just behind the nozzle opening on the high-pressure side which leads to excitation before expansion, causing a problem of nozzle clogging when heavy organic compounds were used. But, in the modified

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nozzle, the sharpened metal tip of the anode has been extended through the nozzle to avoid clogging the nozzle throat by decomposition products and soot deposits of *m*-chlorotoluene. Even though the metal tip exposed less than 1.0 mm outside the end of the nozzle capillary, this improved significantly the clogging problem by partially allowing the excitation to occur after the expansion.

A long copper cathode of 1.5 mm in diameter was placed parallel to the jet direction under the expansion chamber to avoid the arching noise reaching to the PMT detector. The typical discharge current was 5 mA at 1500 V dc potential and was stabilized using a 150 kΩ current limiting ballast resister.

The expansion chamber of six-way cross-type was made of thick walled Pyrex glass tubes of each 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 the expansion with 2.0 atm of backing pressure.

A blue-green colored jet was the evidence of presence of the *m*-chlorobenzyl radicals in the jet. The weak fluorescence emanating from the jet area 5 mm downstream 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 effective resolution of 1 cm^{-1} at the visible region. The spectral region from 18 000 to 26 000 cm^{-1} was scanned at the step of 0.5 cm^{-1} over 1 h to obtain the final spectrum shown in Figure 1. The frequency of the spectrum was calibrated using the He atomic lines[25] observed at the same spectral region as the *m*-chlorobenzyl radicals and is believed to be accurate within 0.5 cm^{-1}.

Since the *m*-chlorobenzyl radical has many vibrational modes and the assignments have not been completed, ab initio calculations on the D_0 state have been performed to help assign the observed vibronic emission spectrum. The calculations were executed with a personal computer equipped with an Intel Pentium 600 MHz processor and 128MB RAM, and with the standard methods included in the GAUSSIAN 98 program for Windows package. The geometry optimization and vibrational frequency calculations were performed at the UHF level and 6-31G* basis set was employed in all calculations.

Results and Discussion

The visible vibronic emission spectra of benzyl-type radicals with C_{2v} symmetry are believed to arise from transitions from the close-lying 2^2B_2 and 1^2A_2 excited states to the 1^2B_2 ground state.[15,26] Two excited electronic states are mixed via vibronic coupling, and ring substitution is expected to affect the energies of the excited states differently.[11] The predicted closeness of the first two excited electronic states of benzyl-type radicals makes it particularly interesting to study perturbation effects on the electronic structure and spectra. In chlorobenzyl radical, the electronic interaction between the chlorine atom and the aromatic ring is undoubtedly of 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. The similarity of electronic energy levels between benzyl and *p*-chlorobenzyl radicals also confirms that the chlorine atom makes insignificant contribution to the electron density of the ring.[15] Thus, *m*-chlorobenzyl radical should exhibit a close relation to those of the benzyl radical, and one may be able to relate the two lowest lying electronic states of *m*-chlorobenzyl radical to parental benzyl $2^2B_2(D_2)$ and $1^2A_2(D_1)$ states.

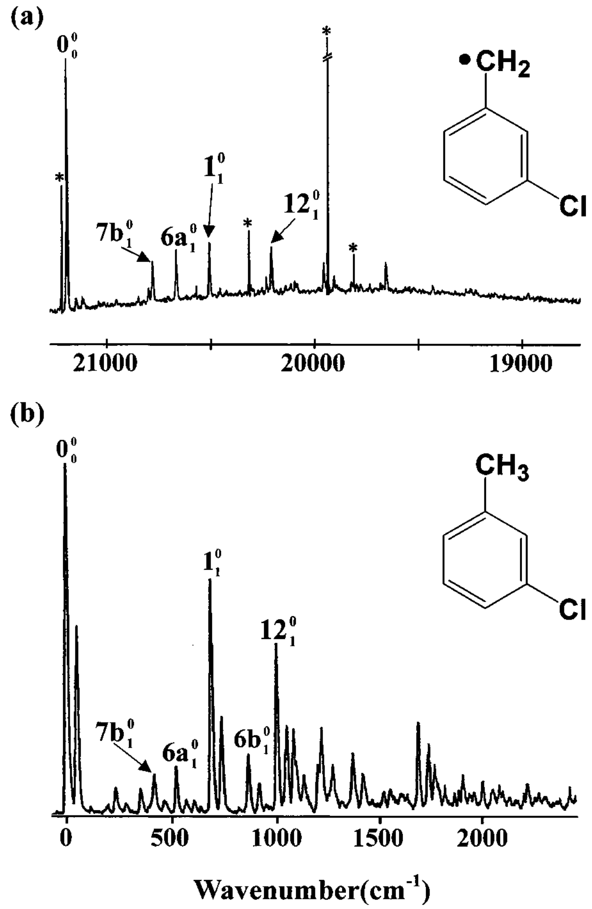

Figure 1. (a) A portion of the vibronic emission spectrum of the $D_1 \rightarrow D_0$ transition of the jet cooled *m*-chlorobenzyl radical which was generated from the *m*-chlorotoluene with a carrier gas He in a corona excited supersonic expansion. The peaks marked by an asterisk indicate the He atomic transitions. (b) The dispersed fluorescence spectrum of *m*-chlorotoluene while pumping the origin band, which was cited from ref 29.

A section of the vibronic emission spectrum of the *m*-chlorobenzyl radical is shown in Figure 1. Most of bands are found in the region of 19500−21500 cm^{-1}. It consists of the strongest vibronic band at 21 194.8 cm^{-1} which is believed to be the origin band of the $D_1 \rightarrow D_0$ transition, followed to lower energies by a series of vibronic bands. But, no bands with noticeable intensity have been found to the blue of the origin, confirming efficient vibrational cooling at the excited electronic states which is an important characteristic feature of the Engelking-type nozzle. The characteristics of benzyl-type radicals generated in CESE have been already identified from comparison with the LIF-DF spectra of *p*-fluorobenzyl radical.[2]

Since most of the bands observed in this work show the doublet character partially separated by ~2.0 cm^{-1} as shown in Figure 2, the frequency of each band was measured at the minimum intensity between the doublet, which is believed to be close to the band origin in comparison with the simulated spectra at 50 K.[27] Of the many bands observed, the origin bands of the visible emission spectra of *o*- and *p*-chlorobenzyl[7] radicals were detected with very weak intensity at 21 041.2 and 21 645.6 cm^{-1}, respectively. The observation of other isomers in a corona discharge has been discussed by Selco and Carrick for the case of xylyl radicals.[10] Although the exact excitation mechanism of CESE source is not known, there is clearly enough energy available to break an α-hydrogen bond and still leave the resulting radical with electronic excitation energy. During the excitation and bond-breaking process of *m*-xylene, the radical

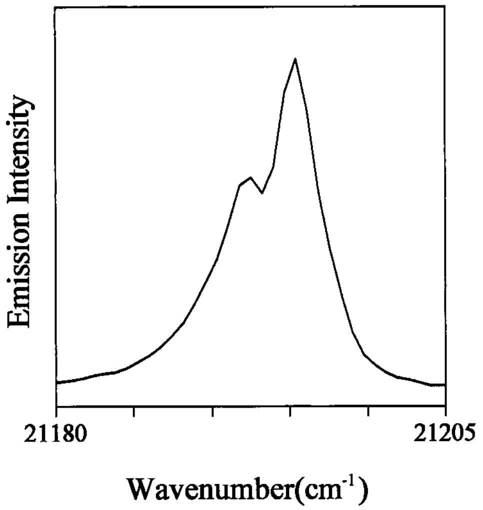

Figure 2. An enlarged view of the band shape at 21194.8 cm^{-1} which is the origin band of the $D_1 \rightarrow D_0$ transition. The band shows a partially splitted doublet character.

may be excited through an intermediate of prismane- or benzvalence-type, which result in the appearance of the *o*- and *p*-xylyl radical isomers in the spectra of the *m*-xylyl radical. But the very weak observation of other isomers in the emission spectrum of *m*-chlorobenzyl radical does not make it possible to identify the origin from either the rearrangement of intermediate or the impurities in the sample. In the CESE spectrum, the frequency difference between the vibronic band and the origin band represents the vibrational mode frequency at the ground electronic state. The vibrational structure of the *m*-chlorobenzyl radical appears in the region of 200−2000 cm^{-1} from the origin band.

The spectrum of the *m*-chlorobenzyl radical does not continue out as far as *m*-chlorotoluene as shown in Figure 1. Most of the modes which are active in the *m*-chlorobenzyl radical but not in the parent are in-plane ring deformation modes. This indicates that interaction between the unpaired electron and the aromatic ring electrons or the D_1 state of *m*-chlorobenzyl has planar structure.

For the direct application of isodynamic approximation, we have also tried to observe vibronic emission spectrum of *m*-chlorotoluene in the transition of $S_1 \rightarrow S_0$ under similar experimental conditions in the UV region, but could only observe the $A^2\Delta \rightarrow X^2\Pi$ transition of CCl which is one of the decomposition fragments of the precursor. Thus, the vibrational mode frequencies given by Varsanyi[28] as well as by Ichimura et al.[29] have been cited in this work. The vibrational mode frequencies of *m*-chlorotoluene in the gas phase was obtained as shown in Figure 1b from the laser dispersed fluorescence spectrum of the jet-cooled *m*-chlorotoluene in the $S_0 \rightarrow S_1$ transition while pumping the origin band. From the comparison, it seems clear that the vibrational structure of both molecules is subjected to the isodynamic approximation which states the correspondence of the vibrational mode frequencies and intensity. This has been already applied to the vibronic assignments of the fluorobenzyl radicals from fluorotoluenes[5,7,30] and the xylyl radicals[8,10,31−33] from xylenes. Thus, most of the vibronic bands of the jet-cooled *m*-chlorobenzyl radical were assigned by comparing with the vibrational mode frequencies of *m*-chlorotoluene as well as an ab initio calculations.

It has been generally accepted that the calculation using GAUSSIAN 98 program at the UHF level with 6-31g* basis set predicts the vibrational mode frequencies within ±10% from the experimental values. From the calculation on the *m*-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 modes of in-plane and out-of-plane vibration, respectively, in the C_s point group. For a better prediction, the calculated values were multiplied by a scaling factor of 0.94 which is the same as the *m*-fluorobenzyl radical.[30]

TABLE 1: Vibrational Frequencies (cm^{-1}) of the *m*-Chlorobenzyl Radical

mode[a]	this work (D_0)	ab initio[b] UHF/6-31G* (D_0)	*m*-chlorotoluene (S_0)	symmetry (C_s)
		origin band: 21 194.8 cm^{-1}		
15	394	396.1	387[c]	a′
7b	413	413.0	409[c]	a′
6a	525	523.2	524[c]	a′
1	686	679.0	687[c]	a′
5	959	946.0	969[d]	a″
12	984	974.1	1002[d]	a′
13	1237	1252.3	1217[d]	a′
3	1287	1300.3	1296[d]	a′

[a] Ref 34. [b] Multiplied by a scaling factor of 0.94. [c] Ref 29. [d] Ref 28.

For the a′ symmetry modes which show strong intensity in the spectrum, the mode 1 of radial skeletal vibration was measured to be 686 cm^{-1} since the frequency of this mode should consist with that of *m*-chlorotoluene (683 cm^{-1}). The calculated value of 679 cm^{-1} coincides well with the observation. All of the benzyl-type radicals examined shows the similarity for this mode.[5,21] The strong band at −525 cm^{-1} from the origin band was assigned to the mode 6a of C−C−C angle deformation. Another deformation 6b which is degenerate in benzene with mode 6a was not observed in this spectrum. The mode of C−Cl stretching vibration was assigned to the strong band at −413 cm^{-1} since both the calculation (413 cm^{-1}) and *m*-chlorotoluene (416 cm^{-1}) agree well with the observation. The mode 15 of in-plane C−H bending vibration was determined to be 394 cm^{-1} which shows excellent agreement with the calculation (396 cm^{-1}) and *m*-chlorotoluene (387 cm^{-1}). The strong band at −984 cm^{-1} was assigned to the mode 12 of C−C−C angle deformation which is fairly insensitive to the substitution. The calculation (974 cm^{-1}) and *m*-chlorotoluene (1002 cm^{-1}) agree with the observation. The mode 3 of C−H in-plane bending was assigned to the weak band at −1287 cm^{-1} from the origin band on the basis of the correspondence between the calculation (1300 cm^{-1}) and *m*-chlorobenzyl (1296 cm^{-1}). The mode 13 of C−Cl stretching vibration was assigned to the moderate band at −1237 cm^{-1} since the calculated intensity and frequency are in accord with the observation.

For the modes with a″ symmetry exhibiting weak intensity in the vibronic emission spectrum, only one vibrational mode was observed with weak intensity. The mode 5 of out-of-plane C−H vibration was assigned to the weak band at −959 cm^{-1}, judging from the calculation and *m*-chlorobenzyl.

From the assignments, the vibrational modes 1 (686 cm^{-1}), 3 (1306 cm^{-1}), 5 (959 cm^{-1}), 6a (525 cm^{-1}), 7b (413 cm^{-1}), 12 (984 cm^{-1}), 13 (1237 cm^{-1}), and 15 (394 cm^{-1}) have been determined. The modes 1 and 12 of strong intensity in the spectrum are also ones involved in the combinations. The combination bands of the $1^0_1 15^0_1$, $1^0_1 7b^0_1$, $12^0_1 15^0_1$, $12^0_1 7b^0_1$, and $12^0_1 13^0_1$ transitions are observed with weak intensity at −1078, −1098, −1392, −1414, and −2221 cm^{-1} from the origin band. The mode frequencies determined in this work are listed in Table 1.

In summary, the jet-cooled *m*-chlorobenzyl radical was generated from *m*-chlorotoluene and vibronically excited with a buffer gas He in a corona excited supersonic expansion using the modified Engelking type nozzle. The vibronic emission spectrum of the *m*-chlorobenzyl radical in the transition of $D_1 \rightarrow D_0$ was recorded using a long path double monochromator in the visible region. The vibrational mode frequencies at the ground electronic state have been obtained by comparing with those of *m*-chlorotoluene and an ab initio calculation.

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