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Vibronic Spectrum of the Jet-Cooled 2,6-Dimethylbenzyl Radical in a Corona Excitation

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A jet-cooled 2,6-dimethylbenzyl radical was generated for the first time from a precursor 2,6-dimethylbenzyl chloride with a large amount of inert carrier gas He in a corona-excited supersonic expansion using a pinhole type glass nozzle. The visible fluorescence emanating from the jet was recorded with a long path monochromator to observe the vibronically resolved jet-cooled emission spectrum. The spectrum was analyzed to obtain accurate electronic transition and active vibrational mode frequencies in the ground electronic state by comparison with those from an ab initio calculation.

Introduction

Although the benzyl radical has received much attention as a prototype of aromatic radicals, alkyl-substituted benzyl radicals have been less studied as large aromatic radicals.[1,2] The earlier works of the xylyl radical in the visible region were reported by Schuler et al.[3] and by Walker and Barrow.[4] Bindley et al.[5,6] made tentative assignments of the vibronic bands from an analysis of the emission spectra of xylyl radicals produced by an electric discharge of the corresponding xylenes.

Selco and Carrick[7] have presented an analysis of the low-resolution vibronic emission spectra of xylyl radicals generated in a corona-excited supersonic expansion, in which many vibrational modes have been identified. Charlton and Thrush[8] have obtained the laser-induced fluorescence spectra of alkyl-substituted benzyl radicals and have measured the lifetime in the excited vibronic states. Lee and colleagues[9−12] have extended the assignments of vibrational modes of xylyl radicals from the vibronic emission spectra. Recently, the controversial assignments of *p*-xylyl radicals have been resolved by an analysis of the vibronic bands from high-resolution emission spectra.[12] The torsional barrier of the internal methyl group has been calculated for the xylyl radicals by Lin and Miller[13] from an analysis of the laser-induced fluorescence excitation and dispersed emission spectra.

The supersonic free jet expansion has been used as a powerful spectroscopic technique for the observation of molecular spectra in the gas phase.[14] The spectral simplification and stabilization associated with the expansion of inert buffer gas cannot usually 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. Of the emission sources developed so far for these purposes, the only one providing enough continuous photon intensity for high-resolution studies of weak transition is the pinhole type glass nozzle,[15,16] which has been widely employed for the observation of the vibronic emission spectra of transient molecules.[17] This has also been applied to the observation of the vibronic emission spectra of many jet-cooled benzyl-type radicals in the gas phase.[18−21]

In this paper, we report for the first time the observation of the dimethyl-substituted benzyl radical, the 2,6-dimethylbenzyl radical, which has been generated from 2,6-dimethylbenzyl chloride in a corona-excited supersonic expansion using a pinhole-type glass nozzle, from which the vibrational modes in the ground electronic state have been assigned by comparison with those from both an ab initio calculation and the precursor.

Experimental Section

The 2,6-dimethylbenzyl radical has been generated and vibronically excited using a technique of a corona-excited supersonic expansion, in which the experimental apparatus is very similar to those described elsewhere.[22] Briefly, it consists of a pinhole type glass nozzle coupled with a high-voltage dc discharge, a portable six-way cross type Pyrex expansion chamber, and a spectrometer for observation of the vibronic emission spectrum.

The radical was generated and vibronically excited in a jet by a corona discharge from the gas mixture of a large amount of inert carrier gas He and 2,6-dimethylbenzyl chloride, which was synthesized in an organic laboratory. The concentration of the precursor in the carrier gas of 2 atm was adjusted for the maximum emission intensity monitored from the strongest band and believed to be about 1% in the gas mixture. The gas mixture was expanded through the 0.4 mm diameter of pinhole type glass nozzle made in this laboratory according to the method described previously.[23] The sharpened long tungsten rod acting as an anode was connected to the high-voltage dc power supply in the negative polarity, in which the axial discharging current was 5 mA at a 1500 V dc potential and stabilized using a 150 kΩ current-limiting ballast resister.

In the original nozzle developed by Engelking,[15,16] 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 are 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 2,6-dimethylbenzyl chloride. Although the metal tip was exposed less than 1.0 mm outside the end of the nozzle capillary, this significantly improved the clogging problem by partially allowing excitation to occur after expansion. The modified

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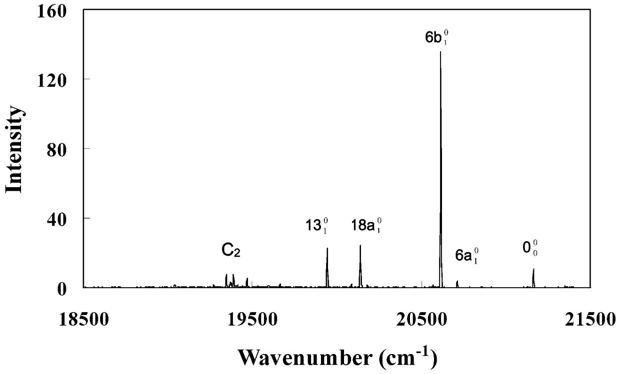

Figure 1. Portion of the vibronic emission spectrum of the jet cooled 2,6-dimethylbenzyl radical in the $D_1 \rightarrow D_0$ transition with the assignment. The weak bands around 19 400 cm^{-1} are from the well-known swan system of the *C*$_2$ which is one of the main fragments in the corona discharge of precursor.

Engelking type nozzle has been applied to the generation of many benzyl-type radicals.

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 a 800 L/min mechanical vacuum pump, resulting in the pressure range 0.5−1.0 Torr during continuous expansion with 2.0 atm of backing pressure. A cathode made of a long copper rod was positioned to be parallel to the jet direction under the expansion chamber to avoid arching noise reaching to the spectrometer.

A bright blue-green jet was the evidence of the presence of the 2,6-dimethylbenzyl radicals in the expansion. The light 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 a resolution of about 2 cm^{-1} in the visible region. The spectral region from 18 000 to 22 000 cm^{-1} was scanned at the step of 1.0 cm^{-1} over 2 h to obtain the final spectrum shown in Figure 1. The wavenumber of the spectrum was calibrated using the He atomic lines[24] observed at the same spectral region as the 2,6-dimethylbenzyl radical and is believed to be accurate within ±1.0 cm^{-1}.

Because the 2,6-dimethylbenzyl 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 package. The geometry optimization and vibrational frequency calculations were performed at the UHF level and the 6-31g* basis set was employed in all calculations.

Results and Discussion

It is apparent that a well-controlled corona discharge of substituted toluenes seeded in a large amount of inert buffer gas predominantly produces corresponding benzyl-type radicals in the excited electronic state. The metastable He atom produced in a corona excitation transfers the excess energy to the substituted toluenes through a collisional process, generating corresponding benzyl-type radicals by the extraction of the chloride atom from the methylene chloride group.

The weak visible emission from the 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 states.[25] Two excited electronic states can be mixed by vibronic coupling, and ring substitution is expected to affect the energies of the excited electronic states differently. Most of the benzyl-type radicals have the lowest excited electronic state of 1^2A_2 except for the *p*-cyanobenzyl radical, which has that of 2^2B_2.[26,27]

In methyl-substituted benzyl radicals, the electronic interaction between the methyl group and the aromatic ring is undoubtedly of the 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, in which the CH_2 group contributes an electron. Thus, the electronic structure of the 2,6-dimethylbenzyl radical should exhibit a close relation to that of the benzyl radical and one may be able to closely relate the two lowest lying electronic states of the 2,6-dimethylbenzyl radical to the parental benzyl $2^2B_2(D_2)$ and $1^2A_2(D_1)$ states.

Figure 1 shows a portion of the vibronic emission spectrum of the 2,6-dimethylbenzyl radical in the $D_1 \rightarrow D_0$ transition, in which many of the strong bands are observed with an excellent S/N in the region of 19 000−21 500 cm^{-1}. The vibrational structure of the radical appears in the region within 2000 cm^{-1} from the origin band because the emission spectrum observed with an Engelking type pinhole nozzle is similar to the dispersed fluorescence spectrum obtained by exciting the origin band of the electronic transition. Thus, the spacing of the vibronic bands from the origin band represents the vibrational mode frequencies in the ground electronic state.

The spectrum consists of the strong origin band of the $D_1 \rightarrow D_0$ transition at 21 164 cm^{-1} (in air), followed to lower energies by a series of vibronic bands. The origin band of the radical does not exhibit the strongest intensity in the emission spectrum. The intensity of the origin band of the benzyl radical at 22 000 cm^{-1} is smaller than those of the $6a^0_1$ and $6b^0_1$ bands as a result of the vibronic coupling between the 2^2B_2 and 1^2A_2 electronic states, which is similar to that of the benzyl radical.[1] However, the absence of bands with observable intensity to the blue of the origin confirms the origin band, resulting from the efficient vibrational cooling at the excited electronic state, which is an important characteristic of an Engelking-type pinhole nozzle.

Because the 2,6-dimethylbenzyl radical belongs to the C_{2v} point group, the bands observed in this study should exhibit the a- or b-type bandshape, depending on the vibrational modes. Other types of benzyl radicals with the same symmetry show distinguishable band shapes in the emission spectra. The bandshapes of *p*-xylyl radical have cleared the controversial assignments of the vibronic bands observed in the emission spectra. Also, the band shapes of many heavy molecules such as benzyl-type radicals have been analyzed to determine the direction of the transition dipole moment by simulating the rotational contour of the bands observed.[30] In this resolution, however, the large amplitude of internal rotation of the two methyl groups in the dimethylbenzyl radical has blotted out the band shape of the vibronic bands observed, as shown in Figure 2.

Thus, the vibronic bands observed were assigned with the help of the known vibrational frequencies of 1,2,3-trimethylbenzene as well as those from an ab initio calculation. From the comparison between two molecules, it seems clear that the vibrational structures in the ground electronic state of both molecules are subjected to isodynamic approximation, which is the correspondence of the vibrational mode frequencies and

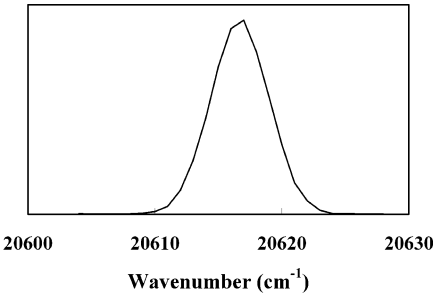

Figure 2. Observed band shape of the strongest band at 20 616 cm^{-1}. The band shows about 5 cm^{-1} of bandwidth (fwhh) due to the internal rotation of two methyl groups.

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

position[a]	intensity[b]	spacing from origin	assignments
21 164	8	0	origin band (0^0_0)
20 712	3	452	$6a^0_1$
20 616	100	548	$6b^0_1$
20 140	18	1024	$18a^0_1$
19 944	17	1220	13^0_1

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

TABLE 2: Vibrational Frequencies (cm^{-1}) of the 2,6-Dimethylbenzyl Radical[a]

		ab initio[c]	precursor	
	this work	UHF/6-31g*	1,2,3-trimethylbenzene[d]	symmetry
mode[b]	(D_0)	(D_0)	(S_0)	(C_{2v})
origin	21164			
6a	452	476.2	485	a_1
6b	548	532.3	539	a_1
18a	1024	1090.3	1095	b_2
13	1220	1249.9	1193	a_1

[a] Measured in air. [b] Reference 31. [c] Multiplied by a scaling factor of 0.95. [d] Reference 28.

transition intensity between the molecules with similar structures. This has already been applied to the vibronic assignments of many benzyl-type radicals.[19−21] The bands observed in this study are listed in Table 1, together with the assignments.

It has generally been accepted that the calculation using the GAUSSIAN 98 program at the UHF level with a the 6-31g* basis set predicts the vibrational mode frequencies within ±10% of the experimental values. The calculation was carried out as described in the Experimental Section. From the calculation for the 2,6-dimethylbenzyl radical, a total of 54 vibrational mode frequencies have been obtained, of which 18, 8, 11, and 17 vibrational modes belong to the A_1, A_2, B_1, and B_2 symmetries in the C_{2v} point group, respectively. The calculated values were multiplied by a scaling factor of 0.95 to match the observed values, as in the case of the 2,6-difluorobenzyl radical. Table 2 lists the observed and calculated vibrational mode frequencies of the 2,6-dimethylbenzyl radical as well as those of the 1,2,3-trimethylbenzene,[28] together with the symmetry of vibrational modes.

The well-resolved bands at −452 and −548 cm^{-1} from the origin band were assigned to the modes 6a and 6b of the C−C−C angle deformation vibration, respectively, which are degenerate at 606 cm^{-1} in benzene. The splitting between 6a and 6b increases with the increasing size of the substituents. For the p-isomer, mode 6b has a higher frequency than mode 6a, but the trend is reversed for the o- and m-isomers. The benzyl radical shows the 6a mode at 524 cm^{-1}, and the 6b modes are observed at 615 cm^{-1} with stronger intensity. The observations are in good agreement with the calculations (476.2 and 532.3 cm^{-1}).

The band at −1024 cm^{-1} from the origin has been assigned to mode 18a of the C−CH_3 in-plane bending mode because the observed intensity and frequency matches with those of the calculation. Modes 18a and 18b are also degenerate in benzene and are fairly insensitive to substitution. The counterpart mode 18b has not been observed because the mode is not active in 1,2,3-trisubstituted benzenes. Calculation shows that the frequency of the 18b component is higher than that of 18a in m- and p-substitution, whereas in o-substitution the case is reversed.

The strong band at −1220 cm^{-1} has been assigned to the mode 20a of the C−CH_3 stretching vibration due to the coincidences with that of the precursor (1248 cm^{-1}) and the calculation (1249.9 cm^{-1}). In this mode the precursor shows a very strong intensity in Raman spectrum.

One of the most important modes, mode 1 of ring breathing has been calculated to locate at −674 cm^{-1} from the origin band. However, in this experiment, this mode was not observed because the two methyl groups have insignificant contribution to the amplitude of vibration.

The several bands at 19400 cm^{-1} with moderate intensity are from the well-known swan system $A^3\Pi_g - X'\ ^3\Pi_u$ of C_2 which is one of the main fragments in the decomposition of hydrocarbons.[29] With increasing discharging voltage, the intensity of C_2 bands increases in the spectrum whereas the intensity of the dimethylbenzyl radical decreases significantly. Thus, the optimization of the discharging condition is crucial in the observation of the vibronic emission spectrum.

In our previous experiment, we have observed several low-frequency sequence bands regularly positioned in the vicinity of every strong vibronic band.[18] The origin of the sequence bands are believed to belong to the combination bands associated with the excited vibrational state in the upper electronic state. Cossart-Magos and Cossart[30] have assigned the $16a^1_0 11^0_1$, $18b^1_1$, 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 the *p*-fluorobenzyl radical in the $D_1 \rightarrow D_0$ transition. But we could not observe these bands with any noticeable intensity because of the limited sensitivity of the spectrometer and weak fluorescence.

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