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Vibronic Spectroscopy of Benzyl-Type Radicals: Observation of Mesityl Radical in the Gas Phase

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We observed, for the first time, the vibronic emission spectrum of the jet-cooled mesityl radical that was formed from mesitylene seeded in a large amount of inert carrier gas helium using a pinhole-type glass nozzle in a corona excited supersonic expansion. The well-resolved vibronic emission spectrum was recorded in the visible region with a long path monochromator. The spectrum was analyzed to identify the origin of the $D_2 \rightarrow D_0$ and $D_1 \rightarrow D_0$ transitions as well as the frequencies of the vibrational modes in the ground electronic state of the mesityl radical by comparison with those of the known data of the precursor and an ab initio calculation.

Introduction

Whereas the benzyl radical,[1] a prototype of the aromatic free radical, has received much attention from spectroscopists, methyl-substituted benzyl radicals have been less studied as large aromatic radicals. Earlier works on the xylyl radicals in the visible region have been published by Schuler et al.[2] and by Walker and Barrow.[3] Bindley et al.[4,5] made vibronic assignments from an analysis of the emission spectra of xylyl radicals produced by an electric discharge of the corresponding xylenes.

Selco and Carrick[6] obtained the low-resolution vibronic emission spectra of xylyl radicals formed in a corona excited supersonic expansion, in which several vibrational modes were clearly identified. Charlton and Thrush[7] obtained the first laser-induced fluorescence spectra of methyl-substituted benzyl radicals and measured their lifetime in the excited vibronic states. Lee and colleagues[8−10] extended the assignments of vibrational modes of xylyl radicals from the vibronic emission spectra. Controversial assignments of *p*-xylyl radicals were resolved by an analysis of the vibronic bandshapes from high-resolution emission spectra.[11] Torsional barrier of the internal methyl rotor for the xylyl radicals was well determined by Lin and Miller[12] from laser induced fluorescence excitation and dispersed emission spectra.

Lee and colleagues have recently presented the vibronic emission spectra[13] of a methyl-substituted benzyl radical, the 2,6-dimethylbenzyl radical, generated from 2,6-dimethylbenzyl chloride using a technique of corona excited supersonic expansion. However, due to the insufficient S/N of the spectra, the assignment given to the transition was not very clear. Lee and colleagues[14] have also recently revised spectroscopic analysis of the 2,6-dimethylbenzyl radical, which analysis utilized the much improved S/N of the emission spectra. They reported the observation of the origin band of the $D_1 \rightarrow D_0$ transition as well as the $D_2 \rightarrow D_0$ transitions. Another isomer of the dimethylbenzyl radical, the 3,4-dimethylbenzyl radical,[15] was reported from the corona discharge of 1,2,4-trimethylbenzene by analysis of the vibrational modes and band shape.

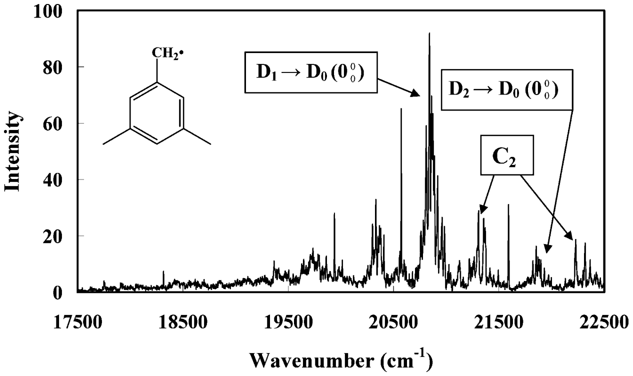

Figure 1. A portion of the vibronic emission spectrum of the jet-cooled 3,5-dimethylbenzyl radical in the $D_1 \rightarrow D_0$ and the $D_2 \rightarrow D_0$ transitions with the assignment. The dense peaks around 21 300 and 22 300 cm^{-1} are from the well-known swan system of the C_2 that may be one of the most abundant fragments in the corona discharge of hydrocarbon.

The fluorescence spectra of the mesityl radical in the solid phase, formed in a photolysis of mesitylene, were reported[16] and compared with the biradical generated in a photolysis of the precursor. Although the origin of the biradical was observed to the blue of the mesityl radical, the accuracy of the origin band of the mesityl radical was limited.

Corona excited supersonic expansion,[17] the technique of corona discharge coupled with supersonic expansion, has been proved to be a powerful spectroscopic technique for observing the vibronic emission spectra of jet-cooled molecular species in the visible and uv region. Electronically excited but rovibrationally cooled species can be generated from spectral simplification, and stabilization of transient species associated with the expansion of inert carrier gas cannot be achieved in any other way. The combination of the supersonic expansion technique with emission spectroscopy has significantly added to and improved the repertoire of spectroscopic studies of molecular species in the gas phase. Of the emission sources developed for these purposes, the one providing enough continuous photon intensity for high-resolution studies of weak transition is the pinhole-type glass nozzle,[18] which has been

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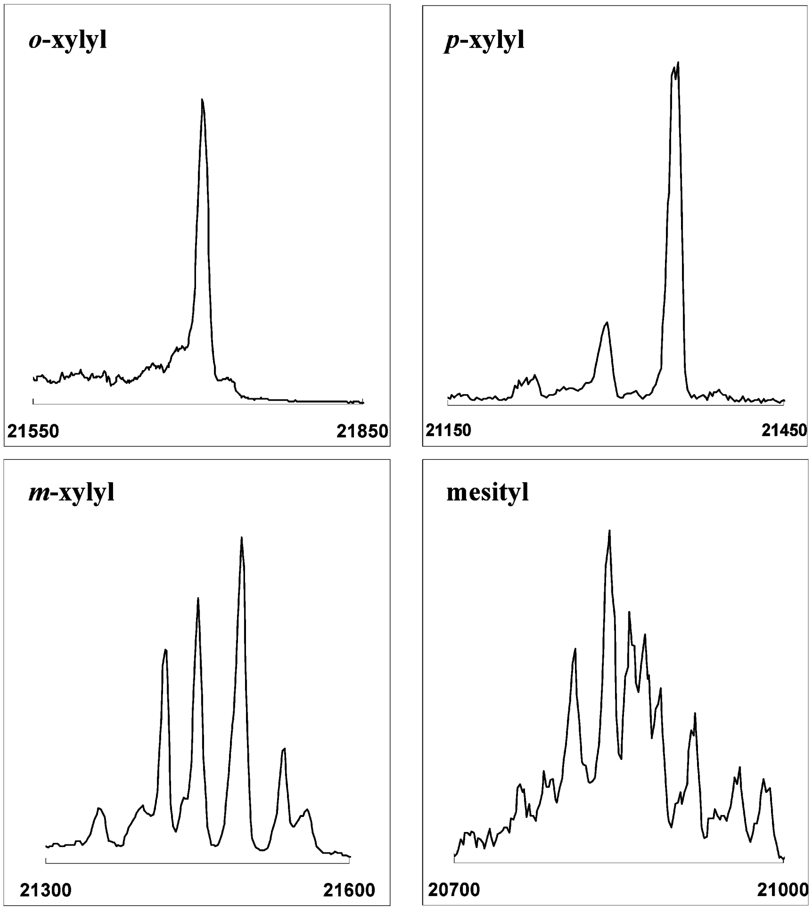

Figure 2. Comparison of the bandshapes observed with those of xylyl radicals. The *m*-xylyl radical shows similar band shape to the 3,5-dimethylbenzyl radical which has two methyl groups at the meta position.

employed for observation of the vibronic emission spectra of transient molecules. This nozzle has also been applied to the vibronic emission spectra of many jet-cooled benzyl-type radicals in the gas phase.[19−22]

In this paper, we report the formation of the jet-cooled mesityl radical from precursor mesitylene in a corona excited supersonic expansion using a pinhole-type glass nozzle, having observed the vibronic emission spectrum. From an analysis of the spectrum, the electronic energies of the $D_2 \rightarrow D_0$ and $D_1 \rightarrow D_0$ transitions and the vibrational mode frequencies in the ground electronic state were obtained by comparison with those from both an ab initio calculation and the precursor.

Experimental Section

The experimental apparatus for observing the vibronic emission spectrum of the jet-cooled mesityl radical in this work is very similar to those described elsewhere.[23] Briefly, it consists of a pinhole-type glass nozzle coupled with a corona discharge, a portable six-way cross-type Pyrex expansion chamber, and a long path monochromator to observe the vibronic emission spectrum.

The vibronically excited mesityl radical was generated from the corona discharge of precursor mesitylene seeded in a large amount of carrier gas He, in which the concentration of the precursor in the gas mixture of 2 bar was adjusted by opening the bypass valve of He gas for the maximum intensity of the strongest origin band monitored in the emission, and was believed to be about 1% in the gas mixture. The discharging gas was expanded through the 0.3 mm diameter orifice of the pinhole-type glass nozzle developed in this laboratory,[18] according to the method described previously. A long, sharpened tungsten rod acting as an anode was connected to a high voltage dc power supply in the negative polarity, in which the axial discharging current of 5 mA at 2000 V was stabilized by using a 150 KΩ current-limiting ballast resister.

The 50 mm diameter six-way cross-type Pyrex expansion chamber was evacuated using an 800 L/min mechanical vacuum pump, resulting in the pressure range of 1.0−2.0 mbar during continuous expansion with 2.0 bar of backing pressure. A long copper rod cathode was positioned under the expansion chamber parallel to the jet direction in order to avoid arcing noise reaching the spectrometer.

A blue-green colored emission was the evidence of the presence of the benzyl-type radicals in the jet, the $D_1 \rightarrow D_0$ transition being known to emit a fairly strong fluorescence in the visible region. Since diatomic fragments generated from the coronal discharge of the precursor, such as CH and C_2, also emit bright fluorescence in the blue region, we tried to minimize the production of fragments by controlling experimental conditions such as orifice size, backing pressure, the voltage applied to the system, and others. The light emanating from the downstream jet area 5 mm 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 1.0 cm^{-1} in the visible region. The spectral region from 17 000 to 23 000 cm^{-1} was scanned at increments of 2.0 cm^{-1}

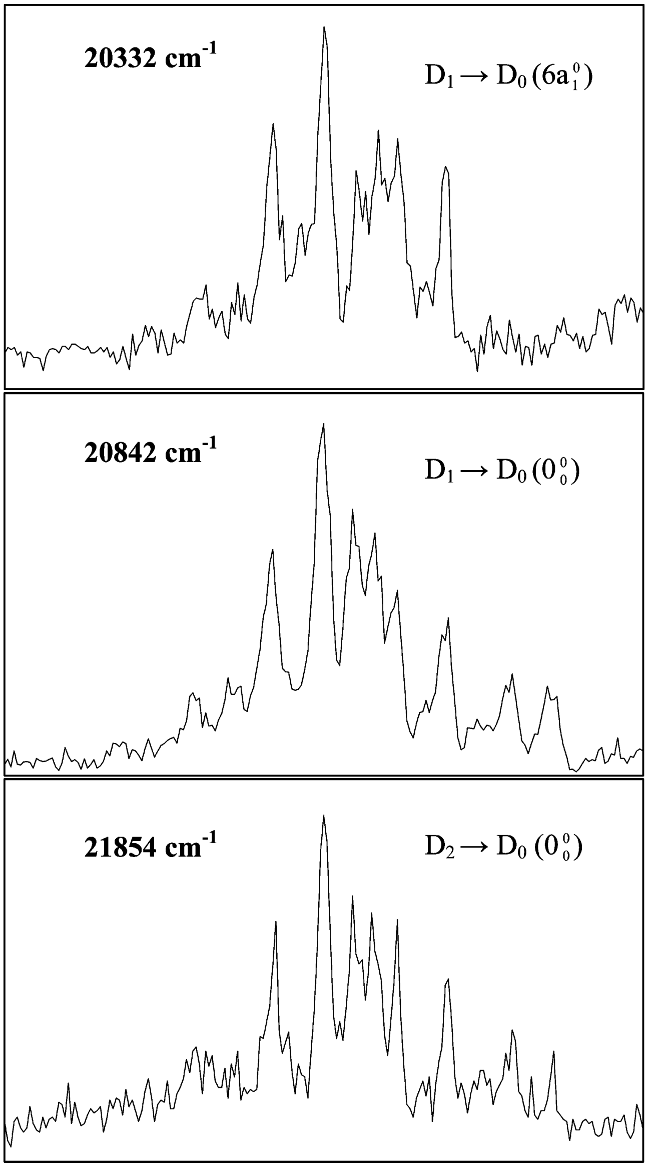

Figure 3. The bandshapes of vibronic bands observed in this work. Three bands show very similarity in band shape, owing to the internal rotation of methyl groups.

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 in the same spectral region as the mesityl radical, and is believed to be accurate to ± 1.0 cm^{-1}.

Since the mesityl radical has many vibrational modes and the mode assignments have not been completely confirmed, ab initio calculations of the ground electronic state were carried out to assist the assignment of the vibronic bands observed. The calculations were executed with a personal computer equipped with an Intel Pentium 2.0 GHz processor and 512 MB RAM, using the standard methods included in the Gaussian 98 program for Windows package. Geometry optimization and vibrational-frequency calculations were performed at the DFT level, and the 6-311g* basis set was employed in all calculations.

Results and Discussion

Since methyl-substituted benzyl radicals[25] have a planar structure with 7 delocalized π electrons, the interaction between the methyl group and the benzene ring is undoubtedly of the second-order compared to that between the methylene group and the benzene ring, in which the methylene group contributes a delocalized π electron by extending conjugation. Thus, the electronic structure of the mesityl radical should exhibit a close relation to that of the benzyl radical, and one might be able to relate the two lowest excited electronic states of the mesityl radical to the parental benzyl radical of the $2^2B_2(D_2)$ and $1^2A_2(D_1)$states.

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

position[a]	intensity	spacing[b]	assignments
21854	m	1012	origin band of $D_2 \rightarrow D_0$
20842	s	0	origin band of $D_1 \rightarrow D_0$
20332	w	−510	$6a_1^0$ of $D_1 \rightarrow D_0$

[a] Measured in air (cm^{-1}). [b] Spacing from the origin band of the $D_1 \rightarrow D_0$ transition (20 842 cm^{-1}).

The visible emission from benzyl-type radicals is believed to arise from transitions to the $1^2B_2(D_0)$ground state from the close-lying $2^2B_2(D_2)$ and $1^2A_2(D_1)$excited electronic states,[26] which can be mixed by vibronic coupling. The vibronic relaxation from the D_2 to D_1 states is so fast that it is extremely difficult to observe transitions resulting from the D_2 state in the emission spectrum. Ring substitution is also expected to affect the energies of the excited electronic states differently as well as the frequencies of the vibrational modes. 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.[27,28]

Figure 1 shows a portion of the vibronic emission spectrum of the mesityl radical formed from the corona discharge of mesitylene in the visible region, in which many of the strong bands were observed with a good S/N in the region of 19 500−22 500 cm^{-1}. Since the precursor should generate only one isomer by extracting a hydrogen atom from the methyl group at any position, we have not tried to identify the species produced by substituting another precursor, such as 3,5-dimethylbenzyl chloride, in a corona discharge. Two methyl substitutions at the meta position were identified, as shown in Figure 2, by comparing the observed bandshapes of the mesityl radical with those of the xylyl radicals, of which the *m*-xyly radical showed similar bandshapes.

The origin band of the $D_1 \rightarrow D_0$ transition was identified as the band with the strongest intensity, because the efficient vibrational relaxation in the D_1 state increases the population of the vibrationless state, from which the molecules emit fluorescence during jet expansion. The identification of the origin band of electronic transition according to its intensity has been well demonstrated in a CESE experiment of benzyl-type radicals. The vibrational structure of the radical in the ground electronic state appears in the region within 2000 cm^{-1} of the origin band since the emission spectrum observed with a pinhole-type glass nozzle is similar to the dispersed fluorescence spectrum obtained by exciting the origin band of the electronic transition.[27,28] Thus, the spacing of the vibronic bands from the origin band represents the vibrational mode frequencies in the ground electronic state. The position of the each vibronic band was measured at the maximum intensity because the simulation of two methyl rotor shows the origin near the maximum height. The simulation spectra of methyl rotor of *p*-xylyl radical are consistent with the observation.[11]

The spectrum consists of two series of vibronic bands starting from those at 20842 and 21854 cm^{-1} (in air), which we strongly believe to be the origin bands of the $D_1 \rightarrow D_0$ and $D_2 \rightarrow D_0$ transitions, respectively, and followed to lower energies by a few vibronic bands. The absence of bands of observable intensity

TABLE 2: Vibrational Frequencies of the Mesityl Radical[a]

mode[b]	this work (D_0)	previous work[c] (D_0)	ab initio[d] B3LYP/6-311g* (D_0)	mesitylene[e] (S_0)	symmetry (C_{2v})
origin ($D_2 \rightarrow D_0$)	21854				
origin ($D_1 \rightarrow D_0$)	20842	20450			
6a	510		520	516	a_1
1			595	579	a_1

[a] In units of cm^{-1} (in air). [b] Ref 38. [c] Data in solid phase. [d] Scaling factor of 1.0. [e] Ref 36.

to the blue of the origin easily confirms the cooling process. The red shift by 1160 cm^{-1} of the origin band of the $D_1 \rightarrow D_0$ transition agrees well with the calculation of 1034 cm^{-1}, according to the substitution effect that has been well applied to symmetric benzyl-type radicals. The calculated value was obtained by taking two meta substitutions into account in the electronic transition of the benzyl radical. The origin band of the $D_1 \rightarrow D_0$ transition in the gas phase at 20 842 cm^{-1} is shifted to the red by 400 cm^{-1} from the position reported in the solid phase, a result which coincides with those of the benzyl, *m*-xylyl, and *p*-xylyl radicals.[31] The shift reflects the limited vibrational motion in the solid phase compared to the free motion in the gas phase.

The origin bands of the D_1 and $D_2 \rightarrow D_0$ transitions of the 2,6-dimethylbenzyl radical have been very recently reported to be located at 20616 and 21164 cm^{-1} in the vibronic emission spectrum, respectively.[14] The intensity of the origin bands of the D_2 and $D_1 \rightarrow D_0$ transitions reflects the energy interval between two excited electronic states that are connected through vibronic coupling. The effect of methyl rotor in intramolecular vibrational energy relaxation was determined by time-resolved spectroscopic technique. Moss and Parmenter[33] reported that relaxation rate is proportional to the density of energy states which is greatly increased by torsional motion of methyl rotor. However, recent study proved that higher order anharmonic resonances between two states may play a pronounced role in determining the relaxation rate of aromatic compounds.[34]

The $D_2 \rightarrow D_0$ transition was assigned by comparison with the bandshapes shown in Figure 3, since the molecule is thought to have similar structures at the higher excited electronic states in benzyl-type radicals. The weak intensity of the origin band of the $D_2 \rightarrow D_0$ transition could be interpreted according to the large energy difference of 1012 cm^{-1} between the two excited electronic states. It has been turned out that the fluorination of methyl rotor has greatly accelerated intramolecular vibrational energy redistribution,[34] providing dimethylbenzyl radicals with a fairly observable intensity from the D_2 state.

Since the mesityl radical belongs to the C_{2v} point group, the bands observed in this study should exhibit the a- or b-type band shape, depending on the vibrational mode. Band shape analysis of the *p*-xylyl radical of the C_{2v} point group clears the controversial assignments of the vibronic bands in the emission spectra. The bandshapes 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 contours of the bands observed.[22,35] The bandshapes of a few vibronic bands in the vibronic emission spectrum of the 2,6-difluorobenzyl radical were compared, confirming the symmetry of vibrational transition. However, the large amplitude of internal rotation of the two methyl groups, and the limited resolution of the spectra blotted out the band shape analysis of the observed vibronic bands, as shown in Figure 3.

Thus, the vibronic assignments were carried out by comparison with not only the known vibrational frequencies of mesitylene but also those from an ab initio calculation. From the comparison between the two molecules, it seems clear that the vibrational structures of both molecules in the ground electronic state are well subject to isodynamic approximation, which determines the correspondence of vibrational-mode frequencies and transition intensity between two aromatic molecules of similar structure. This method has already been applied to the vibronic assignments of many benzyl-type radicals.[20,29] The vibronic bands observed in the present study, together with the assignments, are listed in Table 1.

It has generally been accepted that calculation using the Gaussian 98 program at the DFT level with a 6-311g* basis set predicts the vibrational mode frequencies within, at most, ±10% of the experimental values. From the calculation for the 3,5-dimethylbenzyl radical, a total of 54 vibrational-mode frequencies were 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. Table 2 lists the observed and calculated vibrational mode frequencies of the mesityl radical as well as those of mesitylene,[36] together with the symmetry of the vibrational modes.

The medium intensity band 510 cm^{-1} from the origin band of the $D_1 \rightarrow D_0$ transition was assigned to mode 6a of the C−C−C angle deformation vibration, which is degenerate in mode 6b at 516 cm^{-1} in mesitylene of D_{3h} symmetry. The calculations and precursor showed excellent agreement with the observation listed in Table 2. The splitting between modes 6a and 6b increases with increasing size of the substituents at less symmetric substitution. 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 bandshapes also show similar structure to that of the origin band of the $D_1 \rightarrow D_0$ transition, due to a shared vibronic symmetry. The dependence of bandshapes on the vibrational symmetry has been well demonstrated in the vibronic emission spectrum of the *p*-xylyl radical.

One of the most important modes in benzyl-type radicals, mode 1 of ring breathing, was not observed in that spectrum. The calculation predicts the observation of this mode at 580 cm^{-1} from the origin band. However, the very broad bandshapes due to the internal rotation of the two methyl groups has not allowed a clear identification of the observation. This mode was also observed with weak intensity in the vibronic emission spectrum of the *m*-xylyl radical generated in a CESE.

The several sharp and strong bands resulting from the C_2 and CH fragments were identified at the frequencies reported previously.[37] The C_2 bands are from the well-known swan system in the $A^3\Pi_g - X'^3\Pi_u$ transition, which is known to be one of the most abundant species in the decomposition fragments of hydrocarbons. With increasing discharge voltage, the concentration of the C_2 and CH bands in the medium increases, whereas the production of the mesityl radical decreases significantly. Thus, the optimization of the discharge condition is a crucial factor in the observation of the vibronic emission spectrum. Also, several He atomic lines were observed in the spectrum at frequencies reported previously.

Conclusion

The vibronic emission spectrum of the jet-cooled mesityl radical was observed for the first time from the corona discharge of mesitylene seeded in a large amount of inert carrier-gas helium using a pinhole-type glass nozzle in a CESE, exhibiting the transitions originating from not only the D_1 but also the D_2 state. The observation of the origin band revealed that the transition reported from the solid matrices shifted to the red region by 400 cm^{-1}. From the analysis of the spectrum, we identified only one vibronic band arising from the $D_1 \rightarrow D_0$ transition, owing to the very broad band shape. The observation of the weak transition from the D_2 state can be explained by the inefficient vibronic coupling between the two adjacent electronic states, even though the energy interval between the two excited electronic states is large enough to include many vibrational modes, indicating that the vibronic relaxation is not so efficient in dimethylbenzyl radicals even at energy intervals of 1000 cm^{-1}.

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