Vibronic Spectroscopy of Benzyl-Type Radicals: Jet-Cooled *m*-Cyanobenzyl Radical in the $D_1 \rightarrow D_0$ Transition

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The *m*-cyanobenzyl radical was generated for the first time in a jet from *m*-tolunitrile seeded in a large amount of inert helium carrier gas and vibronically excited using a pinhole-type glass nozzle in a corona excited supersonic expansion. The vibronically well-resolved emission spectrum of the jet-cooled *m*-cyanobenzyl radical in the $D_1 \rightarrow D_0$ transition was recorded with a long-path monochromator in the visible region. The observed spectrum was 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 with those of *m*-tolunitrile.

Introduction

Benzyl radical is a prototypical aromatic free radical, which has been the subject[1−3] of numerous studies. It is well-known that this radical exhibits very weak emission bands in the visible region, because of the transitions from the lowest excited electronic state to the ground electronic state. Particularly, many vibrational modes of the molecule with similar frequencies make it more difficult to identify mode frequencies without high-quality spectra being observed.

Substitutions to the benzene ring are expected to change the electronic energies, the vibrational mode frequencies, and symmetry, which are the important factors in analyzing the spectra, together with the transition intensity. Among many benzyl-type radicals, the xylyl radicals[4−6] have been extensively studied by various methods. The assignments of vibronic bands observed in the visible region have been completed to determine the vibrational mode frequencies in the ground electronic state. Also, the torsional contribution of the methyl rotor has been obtained from an analysis of the rotational contours of the high-resolution Fourier transform (FT) emission spectra.[7]

As for halogen-substituted benzyl-type radicals, the vibrational modes of fluorobenzyl radicals have been assigned using different spectroscopic techniques, such as laser induced fluorescence (LIF)[3,8] and coronal excitation.[9−11] Weakly emitting chlorobenzyl radicals have been recently identified from the vibronic emission spectra,[12−16] in which the sequence of electronic energy of the lowest excited electronic state has shown a similar tendency to the chlorotoluenes.[17]

Cyanobenzyl radicals are interesting molecules in spectroscopy. The analysis of the vibronic emission band shape of the *p*-cyanobenzyl radical has revealed that the lowest excited electronic state is 2^2B_2, which is different from other types of benzyl radicals.[18] Also, several vibrational modes of the *p*-isomer in the ground electronic state have been determined from the analysis of vibronic emission spectrum[19] obtained in the corona discharge. However, other isomers of cyanobenzyl radicals have not been reported in any spectral region, because of the weak fluorescence intensity and lower symmetry.

The supersonic free jet expansion[20,21] has been proven to be a powerful spectroscopic tool for the observation of molecular spectra in the gas phase. The spectral simplification and stabilization associated with the expansion of inert buffer gas cannot be usually obtained in any other ways. The combination of supersonic expansion technique with the emission spectroscopy has had an enormous impact on the repertoire of spectroscopic studies of molecular species that cannot be performed. Of the emission sources developed so far for these purposes, the only one that provides enough continuous photon intensity for high-resolution studies of the weak transition is the pinhole-type glass nozzle,[22,23] which has been widely used for the observation of vibronic emission spectra of transient molecules. This has been applied to the observation of vibronic emission spectra of jet-cooled benzyl-type radicals in the gas phase.[24]

In this study, we report, for the first time, the vibronic emission spectrum of the jet-cooled *m*-cyanobenzyl radical in the $D_1 \rightarrow D_0$ transition, from which the frequencies of vibrational modes in the ground electronic state have been determined by comparison with those from an ab initio calculation and those of *m*-tolunitrile.

Experimental Details

The formation and excitation of the *m*-cyanobenzyl radical in the gas phase have been accomplished using a technique of corona excited supersonic expansion, of which the experimental apparatus is similar to that described elsewhere.[25] Briefly, it consists of a pinhole-type glass nozzle coupled with a high-voltage electric DC discharge, a portable six-way cross-type Pyrex expansion chamber, and a long-path double monochromator for observation of the vibronic emission spectra.

The *m*-cyanobenzyl radical was produced and vibronically excited in a jet from *m*-tolunitrile seeded in a large amount of helium buffer gas in a state of coronal excitation. Reagent-grade *m*-tolunitrile (purchased from Aldrich) was evaporated at room temperature under 2.0 atm of carrier gas in the sample cell. The concentration of the precursor in the carrier gas was adjusted for the maximum emission intensity monitored from the strongest origin band and was believed to be ~1% of the gas

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mixture. The gas mixture was expanded through the 0.4-mm diameter of the pinhole-type glass nozzle that was made in this laboratory, according to the method described previously.[26] The long sharpened stainless-steel rod, which was 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 resistor.

In the original nozzle[21] that was developed by Engelking, the coronal electrode is located just behind the nozzle opening on the high pressure side, which leads to excitation before expansion, causing a nozzle clogging problem when heavy organic compounds were used as the precursor. Thus, we have made the metal tip of the anode extend through the nozzle to reduce the clogging of the nozzle throat by decomposition products and soot deposits of *m*-tolunitrile. Although <1.0 mm of the metal tip was exposed outside the end of the nozzle capillary, this significantly improved the clogging problem[26] by partially allowing excitation to occur after expansion. The modified Engelking-type nozzle has been applied to the generation of many benzyl-type radicals.[27]

The Pyrex expansion chamber was made of thick-walled Pyrex tubes (Chemglass, CG-138-02) 50 mm in diameter. The chamber was evacuated by an 800 L/min mechanical vacuum pump, resulting in a pressure range of 0.5−1.0 Torr during continuous expansion with 2.0 atm of backing pressure. The cathode, which was made of a long copper rod, was positioned to be parallel to the jet direction under the expansion chamber, to buffer the spectrometer from arcing noise.

A bright blue-green color in the jet was evidence of the presence of the *m*-cyanobenzyl radicals. 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) 3.8 cm in diameter placed inside the expansion chamber and focused onto the slit of the monochromator (Jobin Yvon, model U1000) with two 1800 lines/mm gratings and detected with a cooled photomultiplier tube (Hamamatsu, model R649) and a photon counting system. During the scans, the slits were set to 0.100 mm, which provided a resolution of ~1 cm^{-1} in the visible region. The spectral region from 18 000 to 24 000 cm^{-1} was scanned at a rate of 1.0 cm^{-1} over 2 h to obtain the final spectrum that is shown in Figure 1a. The signal-to-noise ratio was mainly limited by the source noise, i.e., the fluctuations in the discharge intensity. We have significantly improved the long-term stability of the source, using a modified pinhole-type nozzle. The wavenumber of the spectrum was calibrated using the He atomic lines[28] observed in the same spectral region as the *m*-cyanobenzyl radical and is believed to be accurate to within ±0.5 cm^{-1}.

For the direct comparison of vibrational mode frequencies, the vibronic spectrum of the *m*-tolunitrile in Figure 1b, which was also vibronically excited in a corona excited supersonic expansion, was taken in the UV region under a similar discharging condition, using a FT spectrometer (Bruker, model IFS-120HR) that was equipped with a quartz-UV beam splitter and a photomultiplier tube (PMT) detector (Hamamatsu, model R166).

The *m*-cyanobenzyl radical has many vibrational modes and the assignments have not been completed; therefore, ab initio calculations of the D_0 state have been performed to assist in the assignment of the vibronic structure of the spectrum. The calculations were executed with a personal computer that was equipped with an Intel Pentium 600 MHz processor and 128 MB RAM, using the standard methods that are included in the GAUSSIAN 98 program for the WINDOWS package. The geometry optimization and subsequent vibrational frequency calculations were performed at the B3LYP level and the cc-pVDZ basis set was used in all calculations. Each vibrational mode was identified through visualization from the change of Cartesian coordinates.

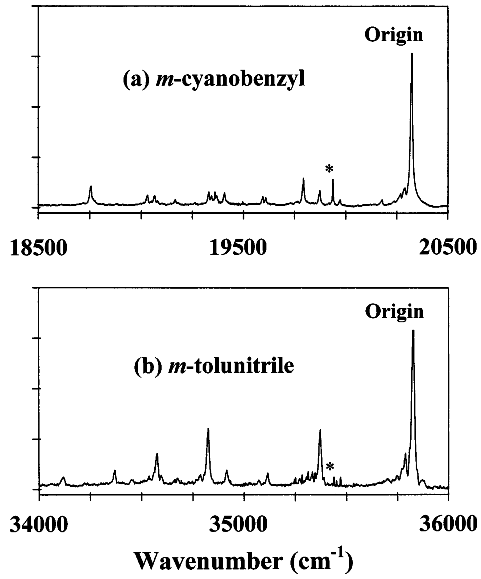

Figure 1. Portion of the vibronic emission spectra of the jet-cooled (a) *m*-cyanobenzyl radical in the $D_1 \rightarrow D_0$ transition and (b) *m*-tolunitrile in the $S_1 \rightarrow S_0$, which were generated from the corona excitation using a pinhole-type glass nozzle. Peaks marked with an asterisk (*) in the spectra indicate the He atomic transitions.

Results and Discussion

Clearly, the well-controlled coronal discharge of substituted toluenes seeded in a large amount of inert carrier gases predominantly produces corresponding benzyl-type radicals in excited electronic states.[2,23] The metastable He atom formed by coronal excitation transfers the excess energy to substituted toluenes through a collisional process to generate corresponding benzyl-type radicals by breaking the α-H bond of the methyl group. The visible emission from benzyl-type radicals is believed to result from transitions to the 1^2B_2 ground state from the close-lying 2^2B_2 and 1^2A_2 excited states, whose energies are affected differently by ring substitution. The lowest excited electronic state of the *p*-cyanobenzyl radical is 2^2B_2, which is different from most benzyl-type radicals of the 1^2A_2 lowest excited electronic state.[18]

In the *m*-cyanobenzyl radical, the electronic interaction between the CN group and the aromatic ring is undoubtedly second-order, compared to that between the methylene group and the benzene ring, because the molecule has a planar structure with seven delocalized π electrons. Thus, the *m*-cyanobenzyl radical should exhibit a close relationship to the benzyl radical and one may be able to relate the two lowest-lying electronic states of the *m*-cyanobenzyl radical to the parent benzyl 2^2B_2 (D_2) and 1^2A_2 (D_1) states.

Figure 1a shows a portion of the vibronically resolved emission spectrum of the *m*-cyanobenzyl radical in the $D_1 \rightarrow D_0$ transition. Most of the strong bands are observed with an excellent signal-to-noise ratio (*S*/*N*) in the region of 18 500−20 500 cm^{-1}. They consist of a strong origin band of the $D_1 \rightarrow D_0$ transition at 20 324.0 cm^{-1} (in air), followed to lower energies by a series of vibronic bands. Diatomic fragments such as CH and CN radicals,[29] which result from the coronal

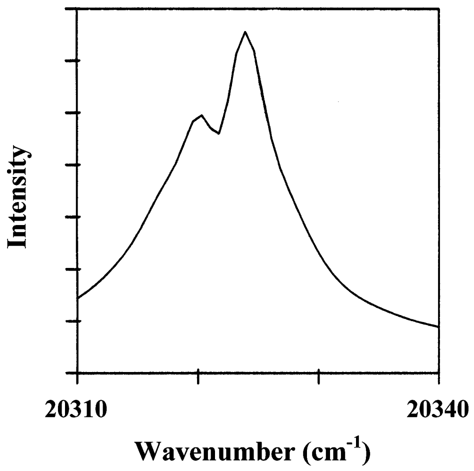

Figure 2. Band shape of the strongest origin band of the jet-cooled *m*-cyanobenzyl radical in the $D_1 \rightarrow D_0$ transition, which shows the doublet partially separated by 3.4 cm^{-1}.

discharge of the precursor, have been identified with a weak intensity at ~23 200 and 23 750 cm^{-1}, respectively. The weak sequence bands in the region of 21 400−21 600 cm^{-1} are from the He$_2$ species at the excited electronic state.[29] The origin bands of the *o*- and *p*-isomers are also observed with weak intensity at the frequencies reported, which are believed to be formed from the small amount of impurities in the sample. The absence of bands with noticeable intensity in the blue region of the origin confirms the efficient vibrational cooling at the excited electronic state, which is an important characteristic of the pinhole-type glass nozzle.[30] Most of the strong bands exhibited the band shapes of a doublet partially separated by an average of 3.4 cm^{-1} in the spectrum, as shown in Figure 2; therefore, the frequency of each band was measured at the maximum intensity of the band.

The vibrational structure of the *m*-cyanobenzyl radical appears in the region of 300−2000 cm^{-1} from the origin band, because the spectrum observed with the pinhole-type glass nozzle is similar to the dispersed fluorescence spectrum obtained by exciting the origin band of the electronic transition, in which the spacing of the vibronic bands from the origin band represents the vibrational mode frequencies in the ground electronic state.

The vibronic bands observed were assigned with the help of the known vibrational frequencies of *m*-tolunitrile, as well as those obtained from an ab initio calculation. The vibrational mode frequencies of *m*-tolunitrile were obtained from well-known data.[31,32] Table 1 lists the bands observed in this study, along with the assignments. From the comparison with *m*-tolunitrile, it seems clear that the vibrational structures in the ground electronic state of both molecules are subject to the isodynamic approximation, which describes the correspondence of vibrational mode frequencies and transition intensity between molecules with similar structure. This has already been applied to the vibronic assignments of many benzyl-type radicals.[8,14]

It has generally been accepted that the calculation using the GAUSSIAN 98 program at the B3LYP level with the cc-pVDZ basis set predicts the vibrational mode frequencies to within ±10% of the experimental values. The calculation has been performed as described in the Experimental Details section. From the calculation for the *m*-cyanobenzyl 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 were multiplied by a scaling factor of 0.980 to match the observed values, as in the case of the *p*-cyanobenzyl radical of 0.945.

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

position	intensity[b]	spacing from origin	assignments[c]
21217.2	5		He atomic line
20800.0	3		
20745.7	5		origin of *p*-isomer
20324.0	100	0.0	origin of *m*-isomer
20291.6	14	32.4	α
20268.9	10	55.1	*β*
20237.3	7	86.7	*γ*
20178.4	9		origin of *o*-isomer
19973.2	6	350.8	15^0_1
19937.4	20		He atomic line
19873.9	12	450.1	$16b^0_1$
19794.2	20	529.8	$6b^0_1$
19766.3	3	557.7	$6a^0_1$
19609.5	7	714.5	1^0_1
19594.9	8	729.1	4^0_1
19408.1	10	915.9	$7b^0_1$
19370.1	8	953.9	5^0_1
19344.7	8	979.3	$6b^0_1 16b^0_1$
19331.6	10	992.4	12^0_1
19264.4	2	1059.6	$6b^{0}_2$[d]
19181.9	2	1142.1	$9b^0_1$
19168.3	4	1155.7	$18b^0_1$
19145.8	1	1178.2	$4^0_1 16b^0_1$
19081.1	2	1242.9	$1^0_1 6b^0_1$
19067.3	7	1256.7	$4^0_1 6b^0_1$
19050.2	2	1273.8	$1^0_1 6a^0_1$
19031.7	8	1292.3	3^0_1
18882.1	1	1441.9	$1^0_1 4^0_1$
18775.8	3	1548.2	$12^0_1 6a^0_1$
18767.2	5	1556.8	$8a^0_1$
18757.2	13	1566.8	$8b^0_1$
18312.4	5		He atomic line
18229.0	3	2095.0	$5^0_1 9b^0_1$
18079.9	3	2244.1	CN

[a] Measured in air (cm^{-1}). [b] Normalized with respect to the strongest origin band. [c] The Greek letters α, *β*, and *γ* indicate the sequence bands observed with the strong origin band. [d] Zero anharmonicity within measurement error. See ref 4.

Table 2 lists the observed and calculated vibrational mode frequencies of the *m*-cyanobenzyl radical, as well as those of *m*-tolunitrile,[31] together with the symmetry of the vibrational modes.

The vibrational mode symmetry of *p*-benzyl-type radicals that belong to the C_{2V} point group can easily be determined from a rotational contour analysis, because the transition dipole moment is parallel to the "*a*" or "*b*" inertial axis for in-plane vibrations. However, the direction of the transition dipole moment of *o*- and *m*-type benzyl radicals cannot be calculated by comparison with simulated spectra, because the transition dipole moment is of a hybrid type. A rotational contour analysis of the origin band of the *o*-xylyl radical shows that the dipole moment is oriented at an angle of +37° or −37°, with respect to the "*b*" inertial axis.[33] For the *m*-cyanobenzyl radical, which belongs to the C_S point group, the vibrational modes have the a′ and a″ symmetry species for in-plane and out-of-plane vibrations, respectively.

Mode 1 of the benzene ring breathing was measured to be 714.5 cm^{-1}, because the frequency of this mode should coincide

TABLE 2: Vibrational Mode Frequencies of the *m*-Cyanobenzyl Radical[a]

	frequency (cm^{-1})			
mode[b]	this work (D_0)	ab initio[c] B3LYP/cc-pVDZ (D_0)	*m*-tolunitrile[d] (S_0)	symmetry (C_S)
origin	20324.0			
1	714.5	713.6	710	a′
3	1292.3	1288.9	1287	a′
4	729.1	719.0	688	a″
5	953.9	976.9	980	a″
6a	557.7	561.2	579	a′
6b	529.8	527.5	524	a′
7b	915.9	912.9	900	a′
8a	1556.8	1548.6	1584	a′
8b	1566.8	1570.0	1601	a′
9b	1142.1	1146.7	1150	a′
12	992.4	983.6	1002	a′
15	350.8	346.5	384	a′
16b	450.1	449.9	460	a′
18b	1155.7	1160.0	1173	a″
CN	2244.1			

[a] Measured in air. [b] From ref 36. [c] Multiplied by a scaling factor of 0.980. [d] From ref 32.

with that of *m*-tolunitrile (712.7 cm^{-1}). The calculation (713.6 cm^{-1}) agrees well with the observation. All the benzyl-type radicals examined show a similarity for this mode.[34] The band with a moderate intensity at 1292.3 cm^{-1} is assigned to mode 3 of the C−H in-plane bending vibration. All three isomers exhibit similar frequencies for this mode. The well-resolved but very weak band at 557.7 cm^{-1} was assigned to mode 6a of the angle deformation of C−C−C. Another angle-deformation vibrational mode—6b, which is degenerate with mode 6a in benzene—was assigned to the very strong band at 529.8 cm^{-1}. The splitting between modes 6a and 6b increases as the size of the substituents increases. For the *p*-isomer, mode 6b has a higher frequency than mode 6a; however, the trend is reversed for the *o*- and *m*-isomers.[34] The observations are in good agreement with the calculation. The band with medium intensity at 915.9 cm^{-1} was assigned to mode 7b of the C−CN stretching vibration, which is also a degenerate pair in mode 7a in benzene. The frequency of degenerate-pair mode 8 is fairly insensitive to substitution. If the symmetric top character of the molecule is dissolved by the substitution, the frequencies of the two vibrational modes 8a and 8b will be different. Modes 8a and 8b of the C−C stretching vibration are assigned to the near bands, at 1556.8 and 1566.8 cm^{-1}, respectively. It is clear that the discrepancy in frequency between the two modes is relatively small and also insensitive to the substitution. In the *m*- and *o*-substitutions, the frequency of the mode 8b component is higher than that of mode 8a, whereas in the *p*-substitution, the case is reversed. The very weak band at 1142.1 cm^{-1} was assigned to mode 9b of the C−H in-plane bending vibration. The degenerate-pair mode 9a at the symmetric top shows a higher frequency in the *p*-isomer, but the trend is reversed in the *o*- and *m*-isomers. The calculation also shows excellent agreement with the observation. The *m*-isomer is the only molecule that gives an active intensity for this mode. The fairly strong band at 992.4 cm^{-1} is assigned to mode 12 of the C−C−C stretching vibration, because the calculated mode analysis shows the same type of vibration. The band with weak intensity at 350.8 cm^{-1} was assigned to mode 15 of the in-plane bending of C−CH_2, which is the next-to-lowest calculated vibrational frequency. Finally, the moderate band at 1155.7 cm^{-1} was assigned to mode 18b of the C−H in-plane bending vibration.

For modes with the a″ symmetry of the out-of-plane vibration, mode 4 of the torsional deformation of C−C was assigned to the band with medium intensity at 729.1 cm^{-1}. The calculated mode shows the out-of-plane motion. Mode 5 of the C−H out-of-plane bending vibration was assigned to the band at 953.9 cm^{-1}, which is the highest frequency of the a″ symmetry. Finally, the fairly strong intensity at 450.1 cm^{-1} was assigned to mode 16b of the torsional deformation of C−C. Both the *p*-isomer and benzonitrile exhibit a frequency similar to that of the *m*-isomer.

Because the molecule has a very similar structure in the excited and ground electronic states, it is difficult to observe significantly intense transitions that lead to the excited vibrational state of the ground electronic state with the clarity shown in other benzyl-type radicals.[15,16,23,24] Thus, only relatively short progressions involving the vibrational mode 6b were identified. The vibrational modes with strong intensity listed above are also active in the combination bands. Many combination bands with fairly strong intensity are observed in the same energy state.

As described previously, we have not observed any band that belongs to the *m*-cyanobenzyl radical to the blue side of the origin band in the spectrum. Instead, several sequence bands have been regularly observed in the vicinity of the origin band at intervals of ∼32, 55, and 87 cm^{-1} from the origin band.

A problem remains in explaining the origin of low-frequency sequence bands in the vicinity of the origin band. Cossart-Magos and Cossart observed several weak bands near the origin band of the *p*-fluorobenzyl radical and assigned them to combination bands that were coupled with the origin band.[35] Fukushima and Obi[3] observed several bands in the vicinity of the strong bands and attributed them as belonging to the van der Waals molecules. However, it seems unlikely in this study that these bands could be attributed to dimers or van der Waals molecules, because the same bands were observed with argon carrier gas, which provides a poor *S*/*N* of the spectrum. Another possibility might be that these bands are due to impurities in the sample, because the sample contains <1% isomers. However, we have detected the origin bands of the *o*- and *p*-cyanobenzyl radicals in the spectrum at the wavenumbers reported previously. The intensity of the origin bands of the other isomers is much weaker than those of the sequence bands coupled with the origin band of the *m*-cyanobenzyl radical. Thus, it does not seem likely that this is a possible explanation for these sequence bands.

A possible explanation of these low-frequency sequence bands might be attributed to the sequence bands associated with the most intensive bands in the spectrum, because the intensity of the sequence bands is proportional to that of the strong vibronic bands. Although Cossart-Magos and Cossart[35] assigned $16a^1_0 11^0_1$, $18b^1_1$, 11^1_1, and $10b^1_1$ to the bands from the origin band of the *p*-fluorobenzyl radical in the $D_1 \rightarrow D_0$ transition observed at −11.3, +7.1, −27.2, and −54.8 cm^{-1}, respectively, it may not be possible at this moment to attempt the assignment of the bands, because of the limited information on vibrational mode frequencies in the excited electronic state.

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

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