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

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The *o*-fluorobenzyl radical was produced in a jet from *o*-fluorotoluene and vibronically excited with a carrier gas (He) in a corona-excited supersonic expansion using a pinhole-type glass nozzle. The vibronically resolved emission spectrum of the jet-cooled *o*-fluorobenzyl radical in the $D_1 \rightarrow D_0$ transition has been recorded with a long-path monochromator in the visible region. The spectrum was analyzed to obtain accurate electronic transition and vibrational mode frequencies in the ground electronic state by comparing with those from an ab initio calculation as well as those of *o*-fluorotoluene.

Introduction

The supersonic free jet expansion has been proven to be a powerful spectroscopic tool for the spectra of molecular species in the gas phase.[1] The spectral simplification and stabilization associated with the expansion of inert buffer gas cannot be usually obtained in any other way. 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 carried out.[2] 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[3,4] which has been widely employed for the observation of vibronic emission spectra of transient molecules.[5] This has been applied to the observation of vibronic emission spectra of jet-cooled benzyl-type radicals in the gas phase.[6−20]

Since the benzyl-type radicals are easily generated from the corresponding toluenes by an electric discharge, Bindley et al. observed the first fluorobenzyl radicals and identified the origin bands of the electronic transition.[21] Charlton and Thrush[22] obtained laser excitation spectra of fluorobenzyl radicals in the visible region with fluorescence lifetime measurements. Of the three isomers, the *p*-fluorobenzyl radical has been extensively studied by rotational contour simulation of the origin band,[23] high-resolution analysis of the vibronic band,[24] and assignments of vibrational modes from laser excitation spectra[25] and vibronic emission spectrum.[8] Recently, Lee and Ahn[17] have reported assignments of vibrational modes of the *m*-fluorobenzyl radical in the ground electronic state from the vibronic emission spectrum. To date, however, no one has reported a full vibronic analysis of the *o*-fluorobenzyl radical.

In this work we report for the first time the vibronic emission spectrum of the jet-cooled *o*-fluorobenzyl radical in the $D_1 \rightarrow D_0$ transition, from which the vibrational mode assignments in the ground electronic state have been accomplished by comparing with those from an ab initio calculation and *o*-fluorotoluene.

Experimental Section

The experimental apparatus employed in this study is similar to those described elsewhere.[8,26] The generation and excitation of the *o*-fluorobenzyl 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 electric dc discharge, a Pyrex expansion chamber, and a spectrometer for the observation of vibronic emission spectrum.

The *o*-fluorobenzyl radical was produced in a jet from *o*-fluorotoluene and vibronically excited with a large amount of buffer gas (He) in a CESE. Reagent grade *o*-fluorotoluene which was purchased from the Aldrich and used without further purification was vaporized at the room temperature under 2.0 atm of carrier gas. The concentration of precursor in the carrier gas was adjusted for the maximum emission intensity monitored from the origin band and believed to be about 1% in the gas mixture. The gas mixture was expanded through the 0.4-mm diameter of the pinhole-type glass nozzle made in this laboratory according to a method described previously.[27] 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.

In the original nozzle developed by Engelking,[3,4] the coronal 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 employed as a precursor. Thus, we have made the metal tip of the anode extend through the nozzle to reduce clogging the nozzle throat by decomposition products and soot deposits of *o*-fluorotoluene. Although the metal tip was exposed less than 1.0 mm outside the end of the nozzle capillary, this improved significantly the clogging problem by partially allowing excitation to occur after expansion. The modified Engelking type nozzle has been applied to the generation of many benzyl-type radicals.[8,14−18]

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 the pressure range 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 to be parallel to the jet direction under the expansion chamber to avoid reaching arching noise to the spectrometer.

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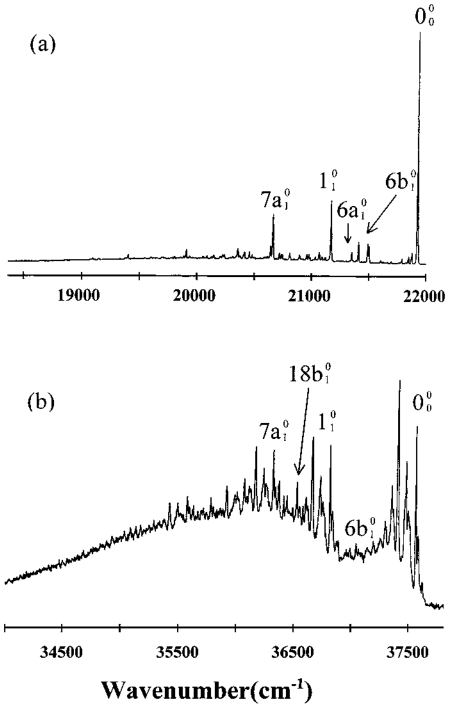

Figure 1. Portion of the vibronic emission spectrum of the jet-cooled (a) *o*-fluorobenzyl radical in the $D_1 \rightarrow D_0$ transition and (b) *o*-fluorotoluene in the $S_1 \rightarrow S_0$ transition with the assignments.

A bright blue-green colored jet was the evidence of the presence of the *o*-fluorobenzyl 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 1 cm^{-1} at the visible region. The spectral region from 18000−24000 cm^{-1} was scanned at a step of 0.5 cm^{-1} over 2 h to obtain the final spectrum shown in Figure 1a. The wavenumber of the spectrum was calibrated using the He atomic lines[28] observed at the same spectral region as the *o*-fluorobenzyl radical and is believed to be accurate within ±0.5 cm^{-1}.

For the direct comparison of vibrational mode frequencies, the vibronic emission spectrum in Figure 1b of the *o*-fluorotoluene, which was vibronically excited in a CESE, was taken in the UV region with the similar discharging conditions using the FT spectrometer (Bruker IFS120HR) equipped with a quartz UV beam splitter and a PMT detector (Hamamatsu R166).

Since the *o*-fluorobenzyl 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 well-known that the well-controlled corona discharge of substituted toluenes with a large amount of inert buffer gases predominantly produces the corresponding benzyl radicals in the excited electronic state.[21,29] 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 states whose energies are affected differently by ring substitution.[30] The fluorobenzyl radicals have 1^2A_2 states as the lowest excited electronic states, such as the benzyl radical, while the *p*-cyanobenzyl radical[16] has a 2^2B_2 state. In the *o*-fluorobenzyl radical, the electronic interaction between the fluorine 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 seven delocalized π electrons. Thus, the *o*-fluorobenzyl 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 the *o*-fluorobenzyl radical to the parental benzyl $2^2B_2(D_2)$ and $1^2A_2(D_1)$ states.

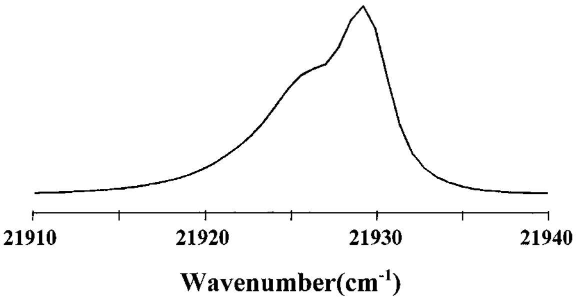

Figure 2. Band shape of the origin band of the *o*-fluorobenzyl radical in the $D_1 \rightarrow D_0$ transition, which shows the doublet partially separated by 3.8 cm^{-1}.

Figure 1a shows a portion of the vibronic emission spectrum of the *o*-fluorobenzyl 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 19000−22000 cm^{-1}. It consists of a strong origin band of the $D_1 \rightarrow D_0$ transition at 21926.8 cm^{-1} (in air), followed to lower energies by a series of vibronic bands. The origin bands of the *m*- and *p*-fluorobenzyl radicals are also observed with weak intensity at the frequencies reported previously, which were generated from the small amount of impurity in the sample. The absence of bands with noticeable intensity to the blue of the origin confirms the efficient vibrational cooling at the excited electronic state which is an important characteristic of the Engelking type nozzle. Since most of the strong bands exhibit the band shapes of doublet partially separated by an average of 3.8 cm^{-1} in the spectrum as shown in Figure 2, the frequency of each band was measured at the minimum intensity between the doublet.

The laser excitation spectra of fluorobenzyl radicals have shown the origin bands of *o*-, *m*-, and *p*-isomers at 21924, 21691, and 21527 cm^{-1} (in vacuum), respectively.[22] Taking vacuum correction into account, the value 21926.8 cm^{-1} determined in this study is in good agreement with that reported previously.

The vibrational structure of the *o*-fluorobenzyl radical appears in the region of 200−2000 cm^{-1} from the origin band since the spectrum observed with an Engelking type 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 at the ground electronic state.

The vibronic bands observed were assigned with the help of the known vibrational frequencies of *o*-fluorotoluene as well as those from an ab initio calculation. The vibrational modes of *o*-fluorotoluene were assigned according to the well-known data.[31] The vibronic emission spectra of the *o*-fluorobenzyl

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

position	intensity[b]	spacing from origin	assignments[c]
21926.8	100	0	origin of *o*-isomer (0_0^0)
21874.6	4	52.2	α
21845.9	3	80.9	β
21787.9	2	138.9	γ
21693.6	1	233.2	origin of *m*-isomer (0_0^0)
21661.0	1	265.8	$10a_1^0$
21622.6	2	304.2	15_1^0
21603.4	2	323.4	
21524.1	1	402.7	origin of *p*-isomer (0_0^0)
21502.4	7	424.4	$16b_1^0$
21490.9	7	435.9	$9b_1^0$
21410.4	9	516.4	$6b_1^0$
21392.2	1	534.6	$16a_1^0$
21351.8	4	575.0	$6a_1^0$
21170.2	25	756.6	1_1^0
21120.9	2	805.9	$1_1^0 + \alpha$
21090.8	2	836.0	$1_1^0 + \beta$
21068.3	3	858.5	$16b_1^0 9b_1^0$
21033.5	1	893.3	$1_1^0 + \gamma$
20986.7	1	940.1	$6b_1^0 16b_1^0$
20977.5	2	949.3	$6b_1^0 9b_1^0$
20958.3	2	968.5	5_1^0
20899.1	2	1027.7	$6b_2^0$
20894.2	3	1032.6	$18b_1^0$
20814.8	2	1112.0	$6a_1^0 16a_1^0$
20807.8	3	1119.0	$18a_1^0$
20746.0	2	1180.8	$1_1^0 16b_1^0$
20734.5	2	1192.3	$1_1^0 9b_1^0$
20718.4	3	1208.4	13_1^0
20662.4	19	1264.4	$7a_1^0$
20641.5	5	1285.3	14_1^0
20613.2	1	1313.6	$7a_1^0 + \alpha$
20595.3	1	1331.5	$1_1^0 6a_1^0$
20583.6	1	1343.2	$7a_1^0 + \beta$
20523.5	1	1403.3	$7a_1^0 + \gamma$
20480.1	2	1446.7	
20456.1	3	1470.7	$9b_1^0 18b_1^0$
20414.3	3	1512.5	1_2^0
20404.9	3	1521.9	$9b_1^0$
20383.9	2	1542.9	$16b_1^0 18a_1^0$
20356.4	4	1570.4	$8a_1^0$
20238.9	2	1687.9	$7a_1^0 16b_1^0$
20226.9	2	1699.9	$7a_1^0 9b_1^0$
20202.5	1	1724.3	$6b_1^0 13_1^0$
20146.3	2	1780.5	$7a_1^0 6b_1^0$
20124.9	1	1801.9	$6b_1^0 14_1^0$
20087.7	1	1839.1	$7a_1^0 6a_1^0$
20052.1	1	1874.7	$1_1^0 18a_1^0$
19906.9	3	2019.9	$1_1^0 7a_1^0$
19885.0	1	2041.8	$1_1^0 14_1^0$
19631.3	1	2295.5	$7a_1^0 18b_1^0$
19600.6	1	2326.2	$1_1^0 8a_1^0$
19401.7	2	2525.1	$7a_2^0$
19093.3	1	2833.5	$7a_1^0 8a_1^0$

[a] Measured in air (cm^{-1}). [b] Normalized with respect to the strongest band. [c] Greek letters α, β, and γ indicate the sequence bands observed with each strong vibronic band.

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

mode[b]	this work (D_0)	ab initio[c] UHF/6-31G* (D_0)	*o*-fluorotoluene[d] (S_0)	symmetry (C_s)
origin	21926.8			
1	757	753.9	746	a′
6a	575	584.9	576	a′
6b	516	528.4	525	a′
7a	1264	1254.0	1233	a′
8a	1570	1598.0	1589	a′
9b	436	441.1	426	a′
13	1208	1185.6	1187	a′
14	1285	1286.8	1298	a′
15	304	309.7	272	a′
18a	1119	1142.1	1112	a′
18b	1033	1034.7	1036	a′
16b	424	416.3	441	a″
16a	535	542.6	536	a″
5	969	967.7	987	a″
10a	266	268.5	288	a″

[a] Measured in air. [b] Ref 34. [c] Multiplied by a scaling factor of 0.961. [d] Ref 31.

radical and *o*-fluorotoluene are compared in Figure 1, together with the vibronic mode assignments. Each vibronic band in the spectrum of *o*-fluorotoluene observed is split into many peaks due to the torsional motion of CH_3.[32] From the comparison, it seems clear that the vibrational structures in the ground electronic state of both molecules are subjected to the isodynamic approximation which 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.[8,14] The bands observed in this work are listed in Table 1, together with the assignments.

The vibrational mode symmetry of *p*-fluorobenzyl and *p*-xylyl radicals in the spectra have been determined from the band shapes observed since 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*-fluorobenzyl radicals since 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.[33] For the *o*-fluorobenzyl 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.

It has been generally accepted that the calculation using the GAUSSIAN 98 program at the UHF level with 6-31G* basis set predicts the vibrational mode frequencies within ±10% of the experimental values. The calculation has been carried out as described in the Experimental Section. From the calculation on the *o*-fluorobenzyl radical, a total of 36 vibrational mode frequencies have been obtained, of which 25 and 11 vibrational modes belong to the a′ and a″ symmetries in the C_s point group, respectively. The calculated values were multiplied by a scaling factor of 0.961 to match the observed values well, as in the case of the *p*-fluorobenzyl radical. Table 2 lists the observed and calculated vibrational mode frequencies of the *o*-fluorobenzyl radical as well as those of *o*-fluorotoluene,[31] together with the symmetry of vibrational modes.

Mode 1 of benzene ring breathing was measured to be 757 cm^{-1} since the frequency of this mode should coincide with that of *o*-fluorotoluene (746 cm^{-1}). The calculation (753.9 cm^{-1}) agrees very well with the observation. The well-resolved bands at 575 and 516 cm^{-1} were assigned to modes 6a and 6b of the C−C−C angle deformation vibration, respectively, which are degenerate in benzene. The splitting between 6a and 6b increases with increasing size of the substituents. For the *p*-isomer, mode 6b has higher frequency than mode 6a, but the trend is reversed for the *o*- and *m*-isomers. The observations are in good agreements with the calculations (584.9 and 528.4 cm^{-1}). The band with very strong intensity at 1264 cm^{-1} was assigned to mode 7a of the C−F stretching vibration, which is also in accord with the calculation (1254.0 cm^{-1}). The mode was also observed with very strong intensity from the *p*-isomer at an analogous frequency. Mode 8a of the C−C stretching was assigned to the band with medium intensity at 1570 cm^{-1} since both the calculation and *o*-fluorotoluene agree with the observation. However, this band may be assigned to mode 7a+15 because of the strong intensity of 7a and a coupling possibility. The strong band at 436 cm^{-1} was assigned to mode 9b of the C−F in-plane bending since the calculation and *o*-fluorotoluene agree well with the observation. On the other hand, mode 9b cannot be observed from the *o*-disubstituted benzene. The band at 1208 cm^{-1} was assigned to mode 13 of the C−F stretching due to coincidence with the calculation (1185.6 cm^{-1}) and *o*-fluorotoluene (1187 cm^{-1}). The sharp band at 1285 cm^{-1} was assigned to mode 14 of the C−C stretching because this mode is independent of the substituent position. The *m*-isomer and 2,6-difluorobenzyl exhibit 1288 and 1268 cm^{-1} for this mode, respectively. Also, the calculation shows excellent agreement with the observation. Mode 15 of the C−F in-plane bending was assigned to the weak band at 304 cm^{-1} since the calculation reveals the lowest wavenumber for a′ symmetry. Modes 18a and 18b, which are degenerate in benzene and fairly insensitive to the substitution, are assigned to the nearest bands at 1119 and 1033 cm^{-1}, respectively. The calculation and *o*-fluorotoluene agree with the observation. In *m*- and *p*-substitution, the frequency of the 18b component is higher than that of 18a, while in *o*-substitution the case is reversed. In this work, the modes with a′ symmetry of in-plane vibration were observed with stronger intensity compared to the out-of-plane modes with a″ symmetry.

For vibrational modes with a″ symmetry, mode 16b was observed with fairly strong intensity at 424 cm^{-1} while the very weak band at 535 cm^{-1} was assigned to the counterpart mode 16a due to coincidence with both the calculation and *o*-fluorotoluene. Mode 5 of the C−F out-of-plane vibration was assigned to the well-resolved band at 969 cm^{-1} because it has excellent agreement with the calculation (967.7 cm^{-1}) which has the highest frequency with a″ symmetry. Finally, mode 10a of the C−F out-of-plane vibration was assigned to the weak but well-resolved band at 266 cm^{-1}, which has excellent coincidence with the calculation (268.5 cm^{-1}). The calculated value is the only one with a″ symmetry in the range of 160−410 cm^{-1}. For planar molecules belonging to C_s point group, $\Delta\upsilon = 1$ transitions are nominally forbidden in the nontotally symmetric a″ modes. However, these transitions presumably are allowed through some type of vibronic coupling.

Relatively long progressions involving the vibrational modes 1 (757 cm^{-1}) and 6b (516 cm^{-1}) were identified. Short progressions involving the vibrational modes 6a (575 cm^{-1}), 7a (1264 cm^{-1}), 8a (1570 cm^{-1}), 9a (436 cm^{-1}), 13 (1208 cm^{-1}), 14 (1285 cm^{-1}), 15 (304 cm^{-1}), 18a (1119 cm^{-1}), 8b (1033 cm^{-1}), 16a (535 cm^{-1}), 16b (424 cm^{-1}), 5 (969 cm^{-1}), and 10a (266 cm^{-1}) have been also observed. The vibrational modes with strong intensity listed above are also active in combination bands.

As described above, we have not observed any band belonging to the *o*-fluorobenzyl radical to the blue of the origin band in the spectrum. Instead, several sequence bands have been regularly observed in the vicinity of every strong vibronic band at an interval of approximately −52, −81, and −139 cm^{-1} from the vibronic band.

A problem remains in explaining the origin of low-frequency sequence bands. Cossart-Magos and Cossart 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.[23] 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.[25] However, it seems unlikely in this study that these bands could be attributed to dimers or van der Waals molecules since the same bands were observed with Ar carrier gas which gives a poor S/N of spectrum. Another possibility might be that these bands are due to impurities in the sample because the sample contains less than a percent of isomers. However, we have detected the origin bands of the *m*- and *p*-fluorobenzyl radicals in the spectrum at the wavenumbers reported previously. The intensity of the origin bands of other isomers is much weaker than those of the sequence bands coupled with the origin band of the *o*-fluorobenzyl radical. Thus, it does not seem likely that this is the 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[23] have assigned $16a^1_0 11^0_1$, $18b^1_1$, 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, it may not be possible at this moment to attempt the assignments of the bands due to the insufficient vibrational mode frequencies at the excited electronic state.

Conclusion

In summary, the *o*-fluorobenzyl radical was generated in the jet from *o*-fluorotoluene with a large amount of carrier gas (He) and vibronically excited in the CESE using a modified Engelking type nozzle. The vibronic emission spectrum of the *o*-fluorobenzyl 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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