Vibronic Assignments of the $S_1 \rightarrow S_0$ Emission Spectrum of the Jet Cooled p-Fluorotoluene

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The p-fluorotoluene was vibronically excited in a jet with a buffer gas He in a corona excited supersonic expansion. The vibronic emission spectrum of the jet cooled p-fluorotoluene in the transition of $S_1 \rightarrow S_0$ has been recorded with a Fourier transform spectrometer in the uv region. The spectrum observed was analyzed to obtain accurate vibrational frequencies in the ground electronic state by comparing with those reported previously. The origin of the low frequency sequence bands observed in this work was discussed. Also, the absence of significant intensity of hot band resulting from the excited vibrational states in the spectrum suggests extensive vibrational cooling in the source.

Introduction

The spectroscopic studies of halogenated aromatic compounds are of considerable interest in both theoretical and experimental chemists because they are believed to play important roles in not only the ozone depletion of the upper atmosphere in the earth but also the reaction mechanism of substituted aromatic compounds.[1] As one of the most suitable candidates, the fluorine substituted aromatic compounds have been extensively investigated since they emit strong fluorescence compared to the other halogenated aromatic compounds. The p-fluorotoluene has been subjects of many spectroscopic studies since it is a typical example of the not only internal rotation but also vibronic interaction.[2-4]

Green has reported the vibrational frequencies and mode symmetry of the p-fluorotoluene from the analysis of infrared and Raman spectra taken in the liquid phase.[5] Varsanyi has extensively discussed and tabulated the vibrational frequencies of the many substituted aromatic compounds in his well-known book including fluorine compounds.[6] Accurate rotational constants and torsional barrier to the internal rotation of p-fluorotoluene were reported by Rudolph and Seiler from the analysis of microwave spectrum.[7-9] Also, Ghosh and coworkers have obtained more accurate vibrational frequencies of p-fluorotoluene in the gas phase from the rovibrational analysis of the rotationally resolved high resolution spectra at the ground electronic state.[10-12] For the vibronic studies of p-fluorotoluene, Cvitas and Hollas[13] have analyzed the rotational contour of the origin band in the $S_1 \rightarrow S_0$ transition and obtained the rotational constants at the ground state as well as the excited electronic state. Also, Seliskar et al.[14] have assigned the vibronic bands from the absorption spectra taken at the room temperature. Okuyama et al.[15] have reported and compared a feature characteristics of internal rotation of the methyl group in the ground and excited electronic states from the fluorescence excitation and dispersed fluorescence spectra of the jet cooled fluorotoluenes. Parmenter and Stone have also discussed the role of internal rotation of methyl group in accelerating intramolecular vibrational redistribution.[16]

Engelking has recently developed a simple nozzle system in a corona excited supersonic expansion, which is useful for the excitation and generation of transient molecules.[17,18] This device has been applied for the observation of the vibronic emission spectra of not only the stable molecules but also the transient molecules.[19,20] As a representative case, Selco and Carrick[21] have determined the vibrational frequencies and symmetry from the rotationally cooled gas phase electronic spectra of toluene and benzyl radical generated in a corona excited supersonic expansion. Recently, Lee and coworkers have significantly improved the quality of the vibronic emission spectra of substituted benzyl compounds by employing a modified nozzle system.[22]

In this study, we report the vibrational frequencies of the p-fluorotoluene at the ground electronic state determined from the analysis of the vibronic emission spectra taken in the uv region and discuss the origin of the low frequency sequence bands observed.

Experimental Details

Figure 1 illustrates the schematic diagram of the corona excited supersonic expansion system used in this work which is similar to those reported previously.[15,19] It consisted of a pinhole type quartz nozzle coupled with corona discharge, a high vacuum expansion chamber, and a spectrometer for the vibronic emission spectrum.

The p-fluorotoluene of the reagent grade was obtained commercially from Aldrich and used without further purification. The compound was vaporized at 25 °C inside the vaporizing vessel made of thick Pyrex glass bottle under 2.0 atm of He gas. The concentration of the p-fluorotoluene in the carrier gas was adjusted using the by-pass valve for the maximum emission intensity and believed to be about 1% in the gas mixture.

The p-fluorotoluene was vibronically excited in a jet with a buffer gas He in a corona excited supersonic expansion. The gas mixture was expanded through the pinhole type nozzle which is similar to that developed by Engelking for the rotational cooling. The nozzle made of the thick walled quartz tube of 12.7 mm outer diameter and 200 mm length was narrowed by flame heating one end to a capillary and coupled with the threaded adaptor (Ace glass model 5027-05) for the gas feeding. The nozzle was terminated abruptly
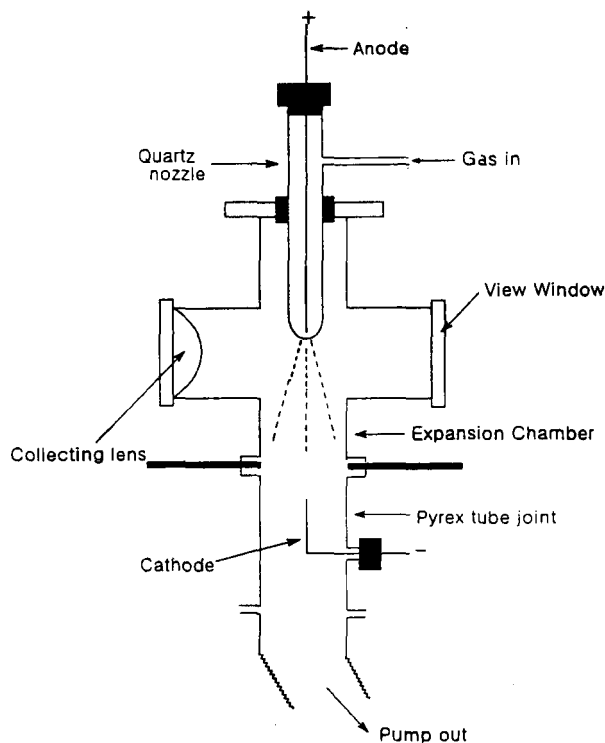
Figure 1. The schematic diagram of the experimental setup used in this work.

Figure 2. A portion of the vibronic emission spectrum of the *p*-fluorotoluene in the transition of $S_1 \to S_0$ recorded with a Fourier transform spectrometer.

on the vacuum side for the free expansion by grinding the one end until the nozzle opening of the appropriate dimension is formed. Of the several nozzles made, we have employed the nozzle of 0.4 mm pinhole diameter which has been proven to be the most effective in this work. The anode made of a stainless steel rod of 1.5 mm in diameter and 300 mm in length was inserted into the nozzle and firmly fixed in the center of the pinhole using a few of teflon holder. In the original nozzle system developed by Engelking, 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 organic compounds were used. Thus, we have modified the metal tip of the anode to be exposed outside the nozzle throat since the corona discharge of the *p*-fluorotoluene produces heavy soot deposits clogging the pinhole. Although, in this study, the length of the metal tip exposed outside the nozzle throat was shorter than 0.5 mm, it significantly improved the stability of the discharge by allowing excitation after expansion.

The anode was connected to a 3.0 kV dc power supply *via* 150. KΩ current limiting ballast resister. The cathode made of copper rod of 100 mm long and 1.5 mm in diameter was placed to be parallel with the jet direction under the expansion chamber to reduce the arching noise which limits the ratio of signal to noise of the spectrum.

The expansion chamber of six-way cross type was made of thick walled Pyrex glass tubes of 50 mm in diameter. The chamber was mounted on a plastic plate and connected to the mechanical vacuum pump through the flexible stainless coupler of the same diameter. The chamber was evacuated by a 600 L/min mechanical vacuum pump, resulting in the pressure range of 1.5-1.8 Torr during the nozzle
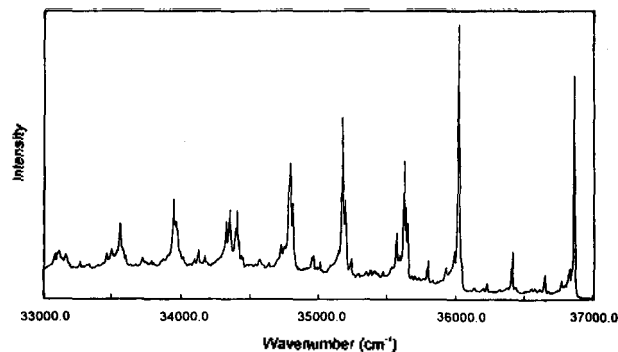
operation with 2.0 atm of backing pressure. The typical discharge current was 5 mA at the 2000 V dc potential. Since the decomposition products increase with the voltage applied for the discharge, we have optimized the condition for the maximum emission intensity of the origin band monitored using a narrow band optical interference filter. With electric discharge of the *p*-fluorotoluene, the *p*-fluorobenzyl radical was also generated in a green jet, which exhibits the vibronic emission spectra in the visible region. The emission from the downstream jet area 5 mm away from the nozzle opening was collected through a combination of two quartz lens placed inside the expansion chamber and focussed onto the emission port of the Fourier transform spectrometer (Bruker IFS-120HR).

The instrument was operated with a quartz-uv beamsplitter, a home-made ac preamplifier and the PMT (Hamamatsu R106UH) detector for photon counter. An optical color filter (Hoya model No. U330) of the spectral bandwidth of 26000-38000 cm^{-1} has been used to block off the strong fluorescence from the carrier gas He in the visible region, which substantially improve the ratio of signal to noise ot the spectra obtained. The spectral region from 15000 to 45000 cm^{-1} was scanned at the resolution of 2.0 cm^{-1}. A total of 1500 scans have been added together over 1 hr. to obtain the final spectrum shown in Figure 2. The frequency of the spectrum was calibrated using the He atomic lines observed at the same frequency region as the *p*-fluorotoluene and is believed to be accurate within 0.05 cm^{-1}.

Results and Discussions

A portion of the vibronic emission spectrum of the *p*-fluorotoluene from the S_1 electronic state to the S_0 ground state is shown in Figure 2. Most of the strong bands are found in the region of 33000-37000 cm^{-1}. Beyond 37000 cm^{-1}, no band with observable intensity has been found while several weak and overlaping bands are observed as a sequence below 33000 cm^{-1}. The band position was measured at the maximum intensity of the peak. The origin band is found at 36872.0 cm^{-1} (in air), which agrees well with 36859.9 cm^{-1} (in vacuum) measured using laser excitation technique.[15] The origin bands of the *o*-, and *m*-fluorotoluenes are reported at 37561.5 and 37385.5 cm^{-1}, respectively.[15]

Figure 3 shows the bandshape of the origin band taken at resolution of 2.0 cm^{-1} which is consisted of two strong
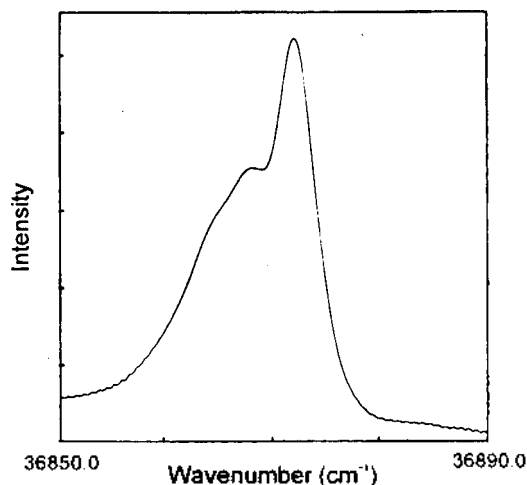
Figure 3. Detailed view of the bandshape of the origin band taken at resolution of 2.0 cm⁻¹.

peaks separated by 2.98 cm⁻¹. Since the origin band belongs to the b-type symmetry, the band origin should be located at the maximum intensity of the higher frequency peak according to simulated spectrum[23] obtained with the rotational constants at 45 K. We have also measured the separations in the five strongest bands and found the average separation to be 2.974±0.2 cm⁻¹. The jet cooled spectrum exhibits the sharp and well-resolved structures compared with the vapor absorption spectra observed by Cave and Thompson,[24] and Joshi[25] at the room temperature. In this spectrum, the origin band shows slightly weak intensity compared to the 1_1^0 band at 36029.4 cm⁻¹ mainly due to the decreasing sensitivity of the detector at the higher frequency and the spectral characteristics of the optical color filter used. In the vibronic emission spectra of the substituted benzene type molecules, the strong intensity of the origin band can be explained on the basis of the similar molecular structures at the both electronic states, leading to the large Franck-Condon factor.

Although the exact mechanism for the excitation is not known in a corona excited supersonic expansion, a wide range of excitation energies exist in the jet as shown by many He atomic emission observed. There are certainly sufficient energy available to excite the pure electronic transition. As a result, p-fluorotoluene molecule initially excited by electron impact must have some excess vibrational energy in the S_1 state. But, no observation of hot bands originating from the higher vibrational states of the S_1 state indicates extensive vibrational cooling of the S_1 state at the nozzle opening. The vibrational cooling effect has been widely observed from the previous works using the Engelking type nozzle system. A listing of the observed peak frequencies, intensity, spacing from the origin band and assignments is presented in Table 1. The vibrational numbering scheme is given according to Wilson.[26] Table 2 summarizes the fundamental vibrational frequencies observed in this work together with those reported previously.

Relatively long progressions involving the vibrational modes 1 (842.6 cm⁻¹), 6b (639.6 cm⁻¹), 7a (1240.5 cm⁻¹), and 13 (1214.5 cm⁻¹) can be observed in the emission spectrum of the p-fluorotoluene. The values of the calculated an-

Table 1. The list of vibronic emission peaks observed from the p-fluorotoluene

Position (cm⁻¹)	Relative intensity	Spacing from the origin (cm⁻¹)	Assignments[a]
36872.0	82.4	0.0	O_0^0
36838.2	12.4	33.8	$\alpha(1)$
36778.2	6.2	93.8	$\alpha(2)$
36655.9	10.9	216.1	$\alpha(3)$
36618.0	3.8	254.0	
36584.0	4.1	288.0	15_1^0
36551.0	3.5	321.0	$10b_1^0$
36446.2	4.4	425.8	$9b_1^0$
36419.4	17.1	452.6	$6a_1^0$
36232.4	5.6	639.6	$6b_1^0$
36203.6	4.2	668.4	$6a_1^0+\alpha(3)$
36141.3	4.27	30.7	12_1^0
36049.1	13.8	822.9	$17b_1^0$
36029.4	100.0	842.6	1_1^0
35995.9	17.4	876.1	$1_1^0+\alpha(1)$
35935.8	11.5	936.2	$1_1^0+\alpha(2)$
35841.5	6.9	1030.5	
35805.2	14.0	1066.8	$1_1^0+\alpha(3)$
35740.8	7.8	1131.2	$1_1^0 15_1^0$
35715.0	7.7	1157.0	$9b_1^0 12_1^0$
35690.5	8.1	1181.5	$6a_1^0 12_1^0$
35657.5	28.0	1214.5	13_1^0
35644.3	32.7	1227.7	$1_1^0 16a_1^0$
35631.5	51.3	1240.5	$7a_1^0$
35598.1	15.6	1273.9	$7a_1^0+\alpha(1)$, $6b_2^0$
35576.9	23.3	1295.1	$1_1^0 6a_1^0$
35479.5	9.9	1392.5	$1_1^0 6a_1^0+\alpha(2)$
35445.1	9.1	1426.9	
35431.1	9.6	1440.9	
35417.9	10.4	1454.1	$7a_1^0+\alpha(3)$
35403.7	9.5	1468.3	
35389.7	10.5	1482.3	$1_1^0 6b_1^0$
35355.6	9.6	1516.4	$1_1^0 6a_1^0+\alpha(3)$
35298.8	9.2	1573.2	$1_1^0 12_1^0$
35242.2	14.0	1629.8	$8a_1^0$
35233.6	13.2	1638.4	$9b_1^0 13_1^0$
35205.6	28.0	1666.4	$7a_1^0 9a_1^0$, $1_1^0 17b_1^0$
35190.6	31.1	1681.4	1_2^0
35180.2	66.9	1691.8	$6a_1^0 7a_1^0$
35148.2	17.1	1723.8	$6a_1^0 7a_1^0+\alpha(1)$
35014.2	14.0	1857.8	$6b_1^0 13_1^0$
34991.4	14.0	1880.6	$6b_1^0 7a_1^0$
34967.9	15.6	1904.1	$6a_1^0 7a_1^0+\alpha(3)$
34955.2	15.6	1916.8	$8a_1^0 15_1^0$
34815.7	34.2	2056.3	$1_1^0 13_1^0$
34799.3	45.1	2072.7	$6a_1^0 7a_1^0 16a_1^0$
34787.3	45.1	2084.7	$1_1^0 7a_1^0$
34752.2	18.7	2119.8	$1_1^0 7a_1^0+\alpha(1)$
34727.5	18.7	2144.5	$6a_2^0 7a_1^0$
34638.0	12.4	2234.0	
34575.8	14.0	2296.2	$1_1^0 7a_1^0+\alpha(3)$
34566.1	14.0	2305.9	$6b_1^0 7a_1^0 9b_1^0$
34537.5	12.4	2334.5	$6b_1^0 7a_1^0 6a_1^0$
34446.7	15.6	2425.3	13_2^0
34436.3	15.6	2435.7	
34418.8	21.2	2453.2	$13_1^0 7a_1^0$

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Table 1. Continued

Position (cm⁻¹)	Relative intensity	Spacing from the origin (cm⁻¹)	Assignments[a]
34407.1	31.1	2464.9	$1_1^0 8a_1^0$
34394.0	24.9	2478.0	$7a_2^0$
34374.5	16.8	2497.5	$1_1^0 8a_1^0 + \alpha(1)$
34362.3	23.3	2509.7	$7a_1^0 + \alpha(1)$
34355.1	32.7	2516.9	1_3^0
34327.5	29.6	2544.5	
34173.4	15.6	2698.6	
34126.8	17.1	2745.2	$13_2^0 10b_1^0$
34097.4	14.0	2774.6	
34014.6	15.6	2857.4	
33992.9	17.1	2879.1	$13_2^0 6a_1^0$
33975.5	24.9	2896.5	$1_2^0 13_1^0$
33961.7	28.0	2910.3	$1_1^0 7a_1^0 17b_1^0$
33950.2	35.8	2921.8	$1_2^0 7a_1^0$
33802.5	12.4	3069.5	
33791.0	14.0	3081.0	
33746.1	14.0	3125.9	
33722.7	15.6	3149.3	
33605.9	15.6	3266.1	$13_2^0 1_1^0$
33578.1	18.7	3293.9	
33566.6	26.4	3305.4	$1_2^0 7a_1^0 16a_1^0$
33505.4	17.1	3366.6	
33471.1	15.6	3400.9	
33278.8	14.0	3593.2	

[a] $\alpha(1)$ $\alpha(2)$, and $\alpha(3)$ denote the sequence bands coupled with vibronic band in the interval of 34, -94, and -216 cm⁻¹.

harmonicity constants for these modes are given in Table 3. Also, short progressions involving the vibrational modes 6a (452.6 cm⁻¹), 8a (1629.8 cm⁻¹), 9b (425.8 cm⁻¹), 10b (321.0 cm⁻¹), 12 (730.7 cm⁻¹), 17b (822.9 cm⁻¹), 15 (288.0 cm⁻¹) have been observed. The vibrational mode 16a (385.1 cm⁻¹) is seen as a combination band only. The modes listed above are also active in combination, as listed in Table 1. The vibrational frequencies have been determined by comparison with the ground state vibrational frequencies obtained from infrared and Raman studies. In most cases, the agreements are within ± 5 cm⁻¹. Seliskar *et al.*[14] also observed the vi-

Table 2. The vibrational frequencies of p-fluorotoluene

Mode	This work (cm⁻¹)	Previous works		Symmetry (C₂ᵥ)
		Gas phase[a]	Liquid phase[b]	
1	842.6	853	844	a₁
7a	1240.5	1237	1223	a₁
13	1214.5	1213	1214	a₁
6a	452.6	448	455	a₁
6b	639.6	639	638	b₂
8a	1629.8		1607	a₁
9b	425.8	424	420	b₂
10b	321.0		340	b₁
12	730.7	730	728	a₁
17b	822.9		816	b₁
15	288.0	287	312	b₂
16a	385.1		404	a₂

[a]Ref.(15), [b]Ref. (6).

Table 3. Anharmonicities of normal vibrational modes of p-fluorotoluene

Mode	Energies/cm⁻¹	ω_e/cm⁻¹	$\omega_e \chi_e$/cm⁻¹
1	842.6	837.6	1.75
6b	639.6	634.3	2.67
7a	1240.5	1237.6	1.45
13	1214.5	1210.8	1.85

brational mode 1 at 842.2 cm⁻¹ from the gas phase vibronic emission spectrum at the high resolution, which is in a good agreement with our observation. Again, as explained above, we have not observed any hot band in the spectrum, confirming extensive vibrational cooling at the nozzle opening. Besides the assignments of vibronic bands, we have also observed several low frequency sequence bands at the interval of approximately -34, -94, and -216 cm⁻¹ from every strong vibronic band.

A problem remains in explaining the low frequency bands that are within 220 cm⁻¹ of the every strong vibronic band. Selco and Carrick have observed the same kinds of bands in the vibronic emission spectra of toluene using a corona excited supersonic expansion, although somewhat different intensity and intervals.[21] It seems unlikely that these bands could be attributed to dimers or van der Waals molecules since the same bands were also observed with Ar carrier gas. A possible explanation of these low frequency bands might be attributed to internal rotations of the methyl group. The torsional frequencies of p-fluorotoluene have been reported by Okuyama *et al.*[15] and Rudolph and Seiler.[9] The values obtained by these two groups for the methyl rotor frequencies and intensities agree very well each other. However, comparison of our low frequency peaks with the frequencies from these other two studies results in very poor correspondences, most of which are more than 10 cm⁻¹ different from the known torsional frequencies. The intensities observed in this study are considerably larger than those previously reported, so this seems an unlikely explanation. Another possibility might be that these peaks are due to impurities in the sample because sample contains less than a percent of isomers. However, we have also detected the origin bands of the o-, m-fluorotoluenes with very weak intensity in the spectrum at the wavelength previously reported. The intensity of the origin bands is much weaker than those of the low frequency sequence bands. Thus, it does not seem likely that this is the best possible explanation for these sequence bands. In the room temperature spectra of toluene using an electric discharge, Kahane-Palius and Leach[27] attributed these low frequency bands to combinations and sequences originating from the vibrationally excited S_1 states of toluene. In the present work, however, no observation of band with significant intensity at the higher frequency beyond the origin band strongly excludes the possibility of the any combination with hot bands. This also confirms extensive vibrational cooling of the S_1 state, resulting in insufficient populations at the vibrationally excited states.

It is possible that these low frequency bands are due to the sequence transitions involving vibrational modes which are not optically active upon a one quantum change in vibrational energy. Cvitas and Hollas[13] have observed the low

frequency sequence structures in the vicinity of the 0-0 band of p-fluorotoluene in the $S_1 \rightarrow S_0$ transition, and made assignments by comparing with the analogous vibrations in p-difluorobenzene and p-chlorobenzene. The sequence band at -34 cm^{-1} is arising from the in-phase mixture of the out-of-bending motions of the methyl group and fluorine atom which has a ground state wavenumber of 144 cm^{-1}. The band observed at the interval of -94 cm^{-1} has been assigned to the out-of-phase and out-of-plane substituent bending mode for which the ground state has 336 cm^{-1}. The sequence band at -216 cm^{-1} is a typical of monosubstituted and para-disubstituted benzenes. It was observed in the phenol spectrum and assigned as a_2 type of C-C twisting vibration(v_{16a}), of which mode p-fluorotoluene has 404 cm^{-1} in the ground state. Also, for this assignment, molecule requires the vibration to be symmetric about the C_2 axis. All of these bands showing weak intensity in the infrared spectrum appear as sequence bands in the vibronic emission spectrum in combination with bands of strong intensity.

Summary

The p-fluorotoluene was vibronically excited in a jet using a modified Engelking type nozzle with buffer gas He in a corona excited supersonic expansion. The vibronic emission spectrum of p-fluorotoluene in the transition of $S_1 \rightarrow S_0$ was recorded using a Fourier transform spectrometer in the uv region. The spectrum was analyzed to obtain more accurate vibrational mode frequencies and anharmonicities at the ground electronic state. Also, the origin of the low frequency sequence bands observed in the spectrum have been discussed and assigned.

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