Vibronic Emission Spectrum of Jet-Cooled *o*-Tolunitrile in a Corona Excited Supersonic Expansion

Chan Ho Park, Gi Woo Lee, and Sang Kuk Lee*

Department of Chemistry and The Chemistry Institute for Functional Materials, Pusan National University, Pusan 609-735, Korea. **E-mail: sklee@pusan.ac.kr*

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We have employed a technique of corona excited supersonic expansion to generate electronically excited but jet-cooled *o*-tolunitrile. The vibronically well-resolved emission spectrum of the jet-cooled *o*-tolunitrile in the $S_1 \rightarrow S_0$ transition was recorded in the uv region using a Fourier transform spectrometer equipped with a Quartz-uv beam splitter. The electronic transition and vibrational mode frequencies in the ground electronic state were accurately determined from the analysis of the spectra observed.

Key Words : Spectroscopy, Vibrational mode, *o*-Tolunitrile

Introduction

Supersonic free-jet expansion has been proven to be a powerful spectroscopic tool for observation of the gas phase molecular spectra in the uv/visible region.[1,2] The spectral simplification and narrow Doppler broadening associated with expansion of inert carrier gas cannot be obtained in any other way. Combination of supersonic jet expansion with emission techniques has significantly extended the repertoire of spectroscopic studies of molecular species.[3]

Of the emission sources developed for these purposes, the one providing enough continuous photon intensity for high resolution spectroscopic studies of weak transition is the pinhole-type glass nozzle that was originally invented by Engelking *et al*.[4,5] and further developed in this laboratory.[6] This simple nozzle has been widely employed to observe the vibronic emission spectra of many molecular species in the gas phase.[3]

The vibrational mode symmetries and frequencies of many benzene derivatives have been tabulated in an excellent book which has been widely employed in the spectroscopic analysis of unknown species. Although the vibrational frequencies and their spectral intensity of stable molecules can be obtained in the field of IR and Raman spectroscopy without difficulty, vibronic spectroscopy coupled with supersonic jet expansion turns out to be a more useful tool for observation of weak transitions because of the larger transition dipole moment in electronic transition. Also, vibrational and rotational cooling during jet expansion significantly reduces the overlapping of bands of large aromatic compounds in the vibronic emission spectrum and makes it possible to accurately determine the vibrational mode frequencies in the ground electronic state.[7]

In this study, we applied the technique of corona excited supersonic expansion to determine the vibrational frequencies in the ground electronic state of *o*-tolunitrile seeded in a large amount of inert carrier gas helium, and from which expansion the vibronic emission spectra of the jet-cooled *o*-tolunitrile was obtained in the $S_1 \rightarrow S_0$ transition with excellent S/N using a Fourier transform spectrometer equipped with a Quartz-uv beam splitter. Very accurate electronic energy and vibrational mode frequencies in the ground electronic state were determined and compared with those from an *ab initio* calculation and the previous results.[8,9]

Experimental Section

It has been known that corona excitation using a high voltage dc discharge vibronically excites benzene-type molecules seeded in a large amount of inert buffer gas. The metastable carrier gas produced in a coronal excitation transfers the excess energy to the molecules through a collisional process.[10]

The *o*-tolunitrile was vibronically excited in a corona excited supersonic expansion in which the experimental apparatus was similar to those described previously.[11-16] The compound *o*-tolunitrile was purchased from Aldrich and was used without further purification. The vapors of the compounds at ambient temperature were entrained in a carrier gas of 2.0 atm He. The concentration of vapor in the carrier gas was adjusted for the maximum emission intensity, monitored from the origin band by controlling the sample temperature and opening the by-pass valve of the carrier gas. The gas mixture was expanded through the 0.3 mm diameter of the pinhole-type glass nozzle made in this laboratory according to the method described previously.[6] A sharpened long tungsten rod acting as an anode was connected to a high-voltage dc power supply of negative polarity, in which the axial discharging current was 5 mA at 2000 V dc potential and stabilized using a 150 kΩ current-limiting ballast resister.

In the original nozzle developed by Engelking,[4,5] the electrode sits just behind the nozzle opening on the high pressure side, and produces excitation before expansion, causing the clogging problem when a heavy organic compounds such as a benzene-type molecule is employed as a sample. Thus, we extended the metal tip of the anode through the nozzle to reduce the clogging of the nozzle throat by decomposition products and sooty deposits of *o*-tolunitrile. Although the metal tip was exposed less than 1.0 mm outside the end of the nozzle capillary, this significantly improved the clogging problem by allowing excitation to partially occur after expansion.

The six-way cross-type expansion chamber made of thick-walled Pyrex tubes of 50 mm in diameter was evacuated by an 800 L/min mechanical vacuum pump, resulting in the chamber pressure of about 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 reduce the arcing noise reaching the spectrometer.

The optical alignment was optimized using a blue-green colored emission, which was the fluorescence of *o*-cyanobenzyl radicals in a jet generated from the corona excitation of *o*-tolunitrile. 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 focussed onto the emission port of a Fourier transform (FT) spectrometer (Bruker IFS-120HR) using two concave mirrors. The instrument was operated with a Quartz-uv beam splitter, a preamplifier (EG&G 113), and a photomultiplier tube (Hamamatsu R166) for photon detection.

Initially, a survey scan was obtained at the low resolution of 2.0 cm^{-1}. Subsequently, after the conditions were optimized, we obtained higher-resolution scans of 0.2 cm^{-1}. The S/N of the spectra was limited mainly by the source noise, that is, the fluctuations in the discharge intensity. One hundred and fifty scans over 1 hour were averaged to obtain the final spectrum shown in Figure 2. The wavenumber of the spectrum, believed to be accurate within ± 0.02 cm^{-1}, was calibrated using the He atomic lines[17] observed in the same spectral region as the *o*-tolunitrile.

Since *o*-tolunitrile has many vibrational modes and the assignments have not been completely confirmed, *ab initio* calculations of the S_0 state were 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 1.2 GHz processor and 512 MB RAM, and using the standard methods included in the Gaussian 98 program for the Windows package. The geometry optimization and calculations of vibrational mode frequency were performed at the DFT level, and a 6-311g basis set was employed in all calculations.

Results and Discussion

Although the exact mechanism of the excitation of *o*-tolunitrile to the higher electronic states in a corona excited supersonic expansion is not known, a wide range of excitation energies might exist,[18] as shown in the He atomic emission lines observed. Therefore, *o*-tolunitrile initially excited by electronic impact must have some excess vibrational energy in the S_1 state. However, non-observation of the hot band originating from the higher vibrational states of the S_1 state indicates extensive vibrational cooling of the S_1 state during the supersonic expansion at the nozzle opening, as shown in Figure 1, which is the important characteristic of a pinhole-type glass nozzle.[19]

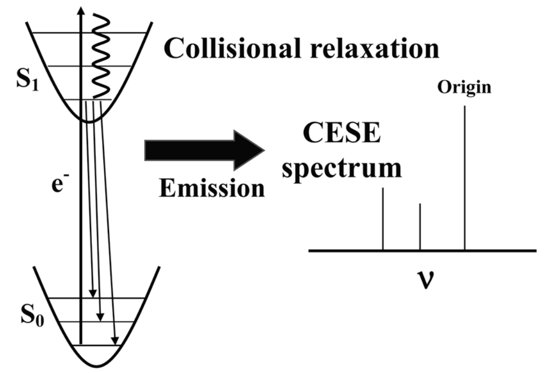

Figure 1. Scheme of CESE spectroscopy for the observation of the vibronic emission spectrum of the jet-cooled *o*-tolunitrile in the $S_1 \rightarrow S_0$ transition. The fast vibrational relaxation in the excited electronic state generates the vibrationally cold spectrum.

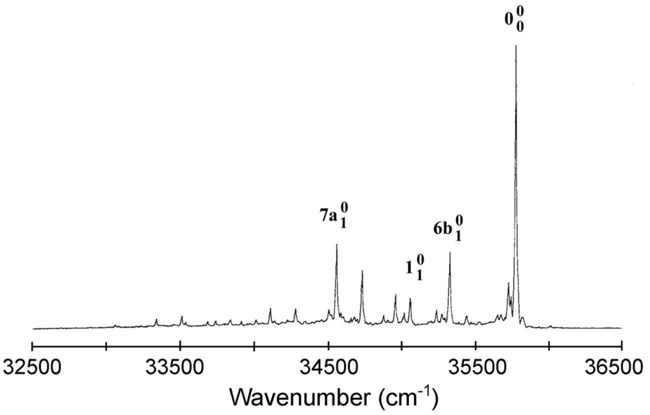

Figure 2. A portion of the CESE vibronic emission spectra of the jet-cooled *o*-tolunitrile in the $S_1 \rightarrow S_0$ transition in the uv region recorded with a FT spectrometer.

The strong uv emission at about 35,000 cm^{-1} is believed to arise from the $S_1 \rightarrow S_0$ transition of benzene derivatives, in which the electronic energies are affected by ring substitution. Figure 2 shows a portion of the CESE vibronic emission spectrum of the *o*-tolunitrile in the $S_1 \rightarrow S_0$ transition. Most of the bands are observed in the region of 33,000-36,000 cm^{-1}. They consist of an origin band of the $S_1 \rightarrow S_0$ transition with a very strong intensity at 35,780.47 cm^{-1} (in air), followed to lower energies by a series of vibronic bands. The origin band of the *o*-isomer was easily identified from a comparison with that of the LIF-DF spectrum[8] observed while pumping the origin band of the electronic transition.

The vibrational structure of the *o*-tolunitrile appears in the region of 200-2000 cm^{-1} from the origin band, since the 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. Thus, 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 mode frequencies of *o*-tolunitrile[8,9] as well as those from an *ab initio* calculation.

For the a' symmetry modes of strong intensity observed in the spectrum, the well-resolved strong bands at 450.5 and 541.1 cm^{-1} from the origin band were assigned, respectively, to modes 6b and 6a of C-C-C angle deformation vibration, which is degenerate in benzene. The splitting between modes 6a and 6b increases with the increasing size of the substituents. For the *p*-isomer, mode 6b has a higher frequency than mode 6a, but this relation is reversed for the *o*- and *m*-isomers. Also, the band of strong intensity at 1,219.8 cm^{-1} was assigned to mode 7a of C-CN stretching vibration, which result accords with the calculation (1,212.0 cm^{-1}). Mode 7a with strong intensity at an analogous frequency was observed for the *p*-isomer.[9] Mode 1 of radial skeletal vibration was measured to be 720.2 cm^{-1}, which accords with the fact that the frequency of this mode is consistent with that reported.[8] This value is slightly less than that of toluene (784 cm^{-1}). The strong band at 819.5 cm^{-1} was assigned to mode 12 of radial skeletal vibration. Modes 8a and 8b of C-C stretching were assigned to the bands at 1,585.5 cm^{-1} and 1,630.9 cm^{-1}, respectively, which are also in good agreement with the calculation. In *para*-substitution, the frequency of the mode 8a component is higher than that of mode 8b, whereas in *o*- and *m*-substitution, the case is reversed.

For the a" symmetry modes that were observed in the spectrum of relatively weak intensity, only two vibrational modes were detected. The moderate intensity band at 761.3 cm^{-1} was assigned to mode 11 of C-H out-of-plane bending vibration. Finally, the band at 392.5 cm^{-1} was tentatively assigned to mode 16a of out-of-plane C-C bending vibration due to the agreement with the calculation.

Relatively long progressions involving vibrational modes 1 (720.2 cm^{-1}), 6a (541.1 cm^{-1}), 6b (450.5 cm^{-1}), 7a (1,219.8 cm^{-1}), and 19a (1,046.5 cm^{-1}) can be observed in the emission spectrum of *o*-tolunitrile. Also short progressions involving vibrational modes 3 (340.9 cm^{-1}), 12 (819.5 cm^{-1}),

Table 1. List of the Observed Vibronic Bands and Their Assignments[a]

position	intensity	spacing[b]	spacing[c]	assignments[d]
36017.19	vw	−236.7		
35940.60	vw	−160.1		
35820.48	w	−40.0		
35780.47	vs	0.0	0.0	origin
35745.93	s	34.5	34.5	α
35727.57	s	52.9	52.9	β
35705.10	w	75.4	75.4	χ
35677.43	w	103.0	103.0	δ
35654.92	w	125.6	125.6	ε
35445.45	m	335.0		
35439.58	m	340.9		3_1^0
35387.95	vw	392.5		$16a_1^0$
35329.94	vs	450.5	0.0	$6b_1^0$
35294.49	m	486.0	35.4	α
35276.45	m	504.0	53.5	β
35239.38	s	541.1	0.0	$6a_1^0$
35204.39	vw	576.1	35.0	α
35060.26	vs	720.2	0.0	1_1^0
35019.16	m	761.3		11_1^0
35007.99	w	772.5	52.3	β
34985.25	vw	795.2	75.0	δ
34961.02	vs	819.5	0.0	12_1^0
34926.25	vw	854.2	34.8	α
34908.08	vw	872.4	52.9	β
34879.50	m	901.0	901.1	$6b_2^0$
34733.97	vs	1046.5	0.0	$19a_1^0$
34699.16	w	1081.3	34.8	α
34681.12	w	1099.4	52.8	β
34657.47	w	1123.0	76.5	χ
34608.46	vw	1172.0	125.5	ε
34588.52	w	1192.0		$9a_1^0$
34560.72	vs	1219.8	0.0	$7a_1^0$
34525.99	vw	1254.5	34.7	α
34508.05	w	1272.4	52.7	β
34458.81	vw	1321.7	101.9	δ
34349.54	vw	1430.9		1_2^0
34289.81	m	1490.7		$19b_1^0$
34242.39	vw	1538.1		$1_1^0+12_1^0$
34195.02	vw	1585.5		$8a_1^0$
34188.59	vw	1591.9		$6a_1^0+19a_1^0$
34149.55	w	1630.9		$8b_1^0$
34111.55	m	1668.9	0.0	$6b_1^0+7a_1^0$
34077.02	vw	1703.5	34.5	α
34058.80	vw	1721.7	52.8	β
34019.11	w	1761.4		$6a_1^0+7a_1^0$
33915.60	m	1864.9		$12_1^0+19a_1^0$
33841.87	m	1938.6		$1_1^0+7a_1^0$
33832.78	vw	1947.7		$6b_2^0+19a_1^0$
33799.14	vw	1981.3		$7a_1^0+11_1^0$
33743.31	m	2037.2		$12_1^0+7a_1^0$
33688.78	m	2091.7		$19a_2^0$
33662.74	vw	2117.7		$6b_2^0+7a_1^0$
33539.81	w	2240.7		CN stretching
33515.08	m	2265.4		$19a_1^0+7a_1^0$
33343.23	m	2437.2		$7a_2^0$
33237.67	vw	2542.8		$6b_1^0+19a_2^0$
33129.79	vw	2650.7		$1_2^0+7a_1^0$
33065.73	w	2714.7		$7a_1^0+19b_1^0$
32895.37	vw	2885.1		$7a_2^0+6b_1^0$
32697.44	vw	3083.0		13_1^0

Table 1. List of the Observed Vibronic Bands and Their Assignments[a]

[a]Measured in air (cm^{-1}). [b]Spacing from the origin band at 35780.47 cm^{-1}. [c]Spacing from the strong vibronic band associated with the sequence bands. [d]Greek letters indicate the sequence bands associated with the strong vibronic band.

9a (1,192.0 cm^{-1}), 19b (1,490.7 cm^{-1}), 8a (1,585.5 cm^{-1}), 8b (1,630.9 cm^{-1}), 13 (3,083.0 cm^{-1}), 11 (761.3 cm^{-1}), and 16a (392.5 cm^{-1}) are observed. The vibrational modes with strong intensity listed above are also active in combination bands. The vibronic bands observed in this work are listed in Table 1, together with the assignments of the transition.

It has been generally accepted that a calculation using the Gaussian 98 program at the DFT level with a 6-311g basis set predicts the vibrational mode frequencies within ± 10% of the experimental values. The calculation was carried out as described in the experimental section. From the calculation of the *o*-tolunitrile, a total of 39 vibrational mode frequencies were obtained, of which 27 and 12 vibrational modes belonged to the a' and a" symmetries, respectively, in the C_S point group. The calculated values were multiplied by a scaling factor of 0.98 to closely match those observed, as in the case of the *m*-cyanobenzyl radical.[20] Table 2 lists the ground electronic state vibrational mode frequencies of the *o*-tolunitrile that were determined in this work, together with the symmetries of the vibrational modes.

The mode symmetry of *p*-isomers is determined from the bandshapes observed, since the transition dipole moment is parallel to the 'a' or 'b' inertial axis for in-plane vibrations. However, the bandshapes cannot easily be distinguished for the *m*- and *o*-isomers, since the transition dipole moment is of the hybrid type. A rotational contour analysis of the origin band of the *o*-xylyl radical showed that the dipole moment is oriented at +37° or −37° with respect to the 'b' inertial axis.[21] For the *o*-tolunitrile that 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.

Also, several sequence bands of very weak intensity were observed in the vicinity of the origin band at the intervals of approximately 34.5, 52.9, 75.4, 103.0, and 108.1 cm^{-1} from the origin band. The same low-frequency sequence bands were also observable in the vicinity of the strong vibronic bands.

Table 2. The Vibrational Frequencies (cm^{-1}) of the *o*-Tolunitrile

mode[a]	this work[b]	*ab initio*[c] B3LYP/6-311g	previous work[d,e]	symmetry (Cs)
Origin	35780.5		35764[e]	
3	340.9	339		a'
6b	450.5	451	450	a'
6a	541.1	545		a'
1	720.2	719	721	a'
12	819.5	815		a'
19a	1046.5	1048		a'
9a	1192.0	1186		a'
7a	1219.8	1212	1220	a'
19b	1490.7	1490		a'
8a	1585.5	1580		a'
8b	1630.9	1613		a'
13	3083.0	3105		a'
11	761.3	771		a"
16a	392.5	391		a"

[a] Ref. 22. [b] Measured in air (cm^{-1}). [c] Multiplied by a scaling factor of 0.98. [d] Ref. 8. [e] Measured in vacuum (cm^{-1}).

A problem remains in explaining the low-frequency bands that are within 200 cm^{-1} of the strong vibronic band. Selco and Carrick[18] observed the same kinds of bands in the vibronic emission spectra of toluene using a corona-excited supersonic expansion, though at a somewhat different intensity and at different intervals. 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, which yields a poor spectral S/N. A possible cause of these low-frequency bands might be attributed to the internal rotations of the methyl group. The torsional frequencies observed in this work agree well with those reported from toluene.

A possible cause 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[10] assigned $16a_0^1 11_1^0$, $18b_1^1$, 11_1^1, and $10b_1^1$ to 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 might not be possible at this moment to attempt the assignments of the bands, due to the insufficient vibrational mode frequencies in the excited electronic state.

In summary, *o*-tolunitrile was vibronically excited by using a technique of corona-excited supersonic expansion. The vibronic emission spectrum of the jet-cooled *o*-tolunitrile in the $S_1 \rightarrow S_0$ transition was recorded with excellent S/N using a Fourier transform spectrometer equipped with a Quartz-uv beam splitter. From an analysis of the spectrum, the accurate electronic transition and vibrational mode frequencies in the ground electronic state were obtained.

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