Assignment of Vibronic Emission Spectra of Jet-Cooled *m*-Tolunitrile

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The technique of corona-excited supersonic expansion was applied to produce electronically excited but rovibrationally cooled *m*-tolunitrile. The well-resolved vibronic emission spectrum of the jet-cooled *m*-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. From an analysis of the spectrum observed, it was confirmed that the electronic transition and vibrational mode frequencies in the ground electronic state were accurately determined.

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

Introduction

The symmetries and frequencies of the vibrational modes of many benzene derivatives were tabulated in an excellent book[1] which has been frequently cited in studies on the spectroscopic analysis of unknown aromatic species. Although the vibrational mode frequencies and their spectral intensity of stable molecules can generally be obtained from IR absorption and Raman spectra, vibronic spectroscopy combined with supersonic free jet expansion has been proved to be a powerful spectroscopic tool for observation of weak transitions, since the large dipole moment change during vibronic transition makes it possible to accurately determine the vibrational mode frequencies in the ground electronic state.[2]

Supersonic free jet expansion has long been employed for observation of the gas phase molecular spectra in the visible/uv region.[3] The narrow Doppler broadening and spectral simplification associated with expansion of inert carrier gas cannot be obtained in any other way. Combination of supersonic jet expansion with emission spectroscopy has significantly extended the repertoire of spectroscopic studies of molecular species in the visible/uv region.[4-7]

Among the emission sources developed for spectroscopic observation, the pinhole-type glass nozzle originally introduced by Engelking *et al.*[8,9] and further developed in this laboratory[10] has been recognized to provide continuous strong photon intensity for high-resolution spectroscopic studies of weak transition. This nozzle has been widely employed to observe the vibronic emission spectra of many aromatic molecular species in the gas phase.

Tolunitriles have been spectroscopically studied by a few experimental methods. The low resolution IR and Raman spectra[11] have revealed vibrational frequencies of strong intensity. The dispersed fluorescence spectra of tolunitriles have been used for determination of the torsional barrier of the methyl group in both the ground and excited electronic states.[12] Recently, the isodynamic rule was applied to the cyanobenzyl radicals to clear the vibrational modes from the known vibronic emission spectra of tolunitriles.[13]

In this study, we observed the vibronic emission spectra of *m*-tolunitrile in the $S_1 \rightarrow S_0$ transition with excellent S/N using a Fourier transform spectrometer equipped with a Quartz-uv beam splitter, coupled with a technique of corona-excited supersonic expansion. From an analysis of the spectrum observed, accurate electronic energy and vibrational mode frequencies in the ground electronic state were determined and compared with those from an *ab initio* calculation and from the previous results.

Experimental Section

It has been demonstrated that the corona discharge of aromatic compounds seeded in a large amount inert carrier gas preferentially generates electronically excited but rovibrationally cooled molecular species in a corona-excited supersonic expansion.[14] The inert carrier gas plays an important role as the energy transferring species for the excitation to higher electronic states as well as for the cooling of rovibrational energy in a jet through a collisional process.[15,16]

The *m*-tolunitrile was vibronically excited in a CESE system using a pinhole-type glass nozzle in which the experimental setup was similar to those described elsewhere.[14] Reagent grade *m*-tolunitrile was purchased from Aldrich and was used without any further purification. The vapors of the compounds were entrained in carrier gas helium of 3.0 atm at room temperature, and the concentration of vapor in the carrier gas was adjusted for the maximum emission intensity, monitored from the strongest 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. A long, sharpened tungsten rod acting as an anode was connected to a high-voltage dc power supply of negative polarity and a 150 kΩ current-limiting ballast resister, in which the axial discharging current was 5 mA at

2,000 V dc potential.

In the corona discharge of heavy aromatic compounds, sticky decomposition fragments clog the nozzle throat, which substantially shortens the duration of stability of corona discharge, so we modified the nozzle system by extending the sharp metal tip of the anode through the nozzle. 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.[10]

The portable six-way cross-type expansion chamber made of thick-walled Pyrex tubes of 50 mm diameter was evacuated by an 800 L/min mechanical rotary vacuum pump, maintaining the chamber pressure of about 1.0 Torr during continuous expansion with 3.0 atm of backing pressure. The maximum backing pressure was limited by the characteristics of the nozzle material, a Pyrex thick-wall glass tube of 12.7 mm diameter in this work. The cathode, a long copper rod positioned under the expansion chamber, was parallel to the jet direction in order to reduce the arcing noise reaching the spectrometer.

For the optical alignment of uv emission, we used a blue-green colored emission of *m*-cyanobenzyl radical that was also generated in a jet from the corona discharge of *m*-tolunitrile. 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 emission port of a Fourier transform 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.

The survey spectrum was obtained at the low resolution of 2.0 cm^{-1}. Subsequently, after the experimental conditions were optimized, we made higher-resolution scans of 0.2 cm^{-1}. The S/N of the spectra was limited mainly by the source noise, the fluctuations in the discharge intensity, so that the stability of the discharging system was believed to be the most important factor in obtaining the higher quality emission spectra. One hundred and fifty scans over 1 hour were averaged to obtain the final spectrum shown in Figure 1. 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 *m*-tolunitrile.
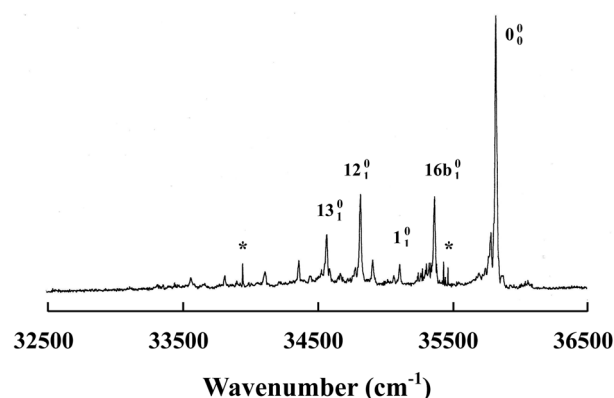
For the assignments of vibrational modes of *m*-tolunitrile, *ab initio* calculations in the S$_0$ state were performed to assist the assignment of the vibronic structure of the spectrum. The calculations were executed with a personal computer equipped with an Intel Pentium IV 1.2 GHz processor and 512 MB RAM, using the standard methods included in the Gaussian 98 program for the Windows package. The geometry optimization and calculations of the vibrational mode frequency were carried out at the DFT level, and a 6-311g basis set was employed in all calculations.
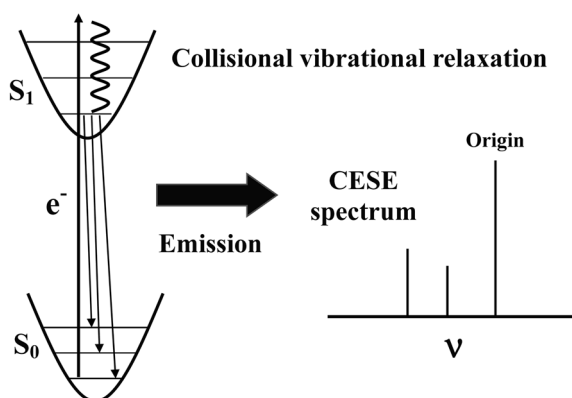
Results and Discussion

The electronic transition from the lowest excited electronic S$_1$ state to the ground electronic S$_0$ state is believed to be observed in the 35,000 cm^{-1} region for benzene derivatives.[18] Although the exact mechanism of *m*-tolunitrile in excitation to the higher vibronic states is not known in a CESE system, a wide range of excitation energies might exist in a corona discharge observed in He atomic emission lines. Therefore, *m*-tolunitrile initially excited to the S$_1$ state in collision with metastable helium atoms must have some excess vibrational energy. However, no observation with noticeable intensity of the hot band originating from the higher vibrational states belonging to the S$_1$ state indicates efficient vibrational cooling in the S$_1$ state during supersonic jet expansion at the nozzle opening. The cooling of rovibrational energy is an important characteristic of a pinhole-type glass nozzle.

Figure 1 shows a portion of the CESE vibronic emission spectrum of the *m*-tolunitrile in the S$_1 \rightarrow$ S$_0$ transition, in which spectrum most of the vibronic bands are observed with excellent S/N 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 the strongest intensity at 35,828.60 cm^{-1}, followed to lower energies by a series of vibronic bands. The energy of electronic states is also affected by ring substitution. The origin band of the *m*-isomer was easily identified from a comparison with that of the LIF-DF spectrum observed while pumping the origin band of the electronic transition.

Since the spectrum observed with a pinhole-type glass nozzle is similar to the dispersed fluorescence spectrum obtained by pumping the origin band of the electronic transition, the vibrational structure of the *m*-tolunitrile in the ground electronic state appears in the region of 200-2,000 cm^{-1} from the origin band. The spacing from the vibronic bands to the origin band represents the vibrational mode frequencies in the ground electronic state, as indicated in

Figure 1. A portion of the vibronic emission spectrum of the jet-cooled *m*-tolunitrile in the S$_1 \rightarrow$ S$_0$ transition recorded with a FT spectrometer. The molecules were vibronically excited in a corona-excited supersonic expansion using a pinhole-type glass nozzle. The peaks marked with an asterisk in this spectrum indicate the He atomic transitions.

Figure 2. Scheme of CESE spectroscopy for observation of the vibronic emission spectrum of the jet-cooled *m*-tolunitrile in the $S_1 \rightarrow S_0$ transition. The efficient collisional relaxation of vibrational energy in the lowest excited electronic (S_1) state generates the electronically hot but rovibrationally cold species.

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

position	intensity	spacing[b]	spacing[c]	assignments[d]
34880.88	vw	−52.3		
35874.60	vw	−46.0		
35828.60	vs	0.0		Origin
35810.20	m		18.4	α
35789.80	m		38.8	β
35776.60	w		52.0	γ
35749.90	w		78.7	δ
35727.50	w		101.1	ε
35702.90	w		125.7	ξ
35372.90	vs	455.7		$16b_1^0$
35355.08	w		17.8	α
35347.23	w			He atomic line
35272.40	w	556.2		$16a_1^0$ /C-CN in-plane bending
35115.90	m	712.7		1_1^0
35072.50	w	756.1		11_1^0
34916.30	m	912.3		$18a_1^0$
34825.40	vs	1003.2		12_1^0
34805.20	w		20.2	α
34787.70	w		37.7	β
34748.60	vw		76.8	δ
34677.30	vw	1151.3		$18b_1^0$
34596.10	w	1232.5	81.2	δ
34576.10	s	1252.5		13_1^0
34459.50	vw	1369.1		$16b_1^0 18_1^0$
34370.60	m	1458.0		$19a_1^0$
34120.90	w	1707.7		$16b_1^0 13_1^0$
33954.40	m			He atomic line
33913.50	vw	1915.1		$12_1^0 18a_1^0$
33823.60	w	2005.0		12_2^0
33573.10	vw	2255.5		$12_1^0 13_1^0$

[a]Measured in vacuum (cm^{-1}). [b]Spacing from the origin band at 35828.60 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.

Figure 2. The observed vibronic bands were assigned with the help of the known vibrational-mode frequencies of *m*-tolunitrile as well as those from an *ab initio* calculation.

For the a' symmetry of the in-plane vibrational modes, the medium intensity band at 712.7 cm^{-1} was assigned to mode 1 of ring breathing radial skeletal vibration, one of the most important modes in benzene-type molecules. That value is slightly less than that of toluene (784 cm^{-1}) because of the substitution of CN group instead of an H atom. Modes 18a and 18b of C-CH$_3$ in-plane bending vibration was assigned to the medium intensity band at 912.3 cm^{-1}, and very weak band at 1151.3 cm^{-1}, respectively, which are also degenerate in benzene. The splitting between modes 18a and 18b increases with the size of the substituents.[1] For the *p*-isomer, mode 18a has a higher frequency than mode 18b, but this trend is reversed for the *o*- and *m*-isomers. The very strong intensity of band at 1,003.2 cm^{-1} from the origin was assigned to mode 12 of the C-C-C stretching vibration. The observation of about 1,000 cm^{-1} for mode 12 indicates the possibility of weak coupling with mode 1. That calculation agrees well with the observation for this mode. Also, low frequency sequence bands similar to those observed near the origin band were observed in the vicinity of this band, as shown in Table 1. The strong band at 1,252.5 cm^{-1} from the origin was assigned to mode 13 of C-CH$_3$ stretching vibration. This mode is easily coupled with radial skeletal vibrations of modes 1 and 12 for benzene-type molecules with light substituents. The medium intensity band at 1458.0 cm^{-1} from the origin was assigned to C-C stretching vibrational mode 19a which is not very sensitive to substitution except for heavy halogen. Another pair mode 19b should be observable at slightly higher wavenumber for *m*-substitution., which was not observed in this work.

For the a" symmetry of the out-of-plane vibration modes, only three modes were detected from the spectrum observed. The well-resolved bands at 456 and 556 cm^{-1} from the origin band were assigned, respectively, to modes 16b and 16a of out-of-plane skeletal vibrations, which modes are also degenerate in benzene. The band at 556 cm^{-1} also coincides with the C-CN in-plane bending vibration. The splitting between modes 16a and 16b increases with the size of the substituents. For the *p*-isomer, mode 16b has a higher frequency than mode 16a, but this trend is reversed for the *o*- and *m*-isomers. Finally, the weak band at 756.1 cm^{-1} from the origin was assigned to mode 11 of C-H out-of-plane vibration. This mode is very active in *p*-isomer, whereas it is observed to be weak in *o*- and *m*-isomers. However, the frequency of this mode is less sensitive to the position of substituents.[1]

Relatively short progressions involving vibrational modes 16b (455.7 cm^{-1}) and 12 (1,003.2 cm^{-1}) could be observed in the vibronic emission spectrum of *m*-tolunitrile. The vibrational modes of strong intensity are also active in combination bands. In this work, several combination bands were also observed with weak intensity at the calculated positions, which are listed in Table 1, together with the assignments of the transition.

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

Mode[a]	This work[b]	*ab initio*[c] B3LYP/6-311g	Previous work[d]	Symmetry (Cs)
Origin	35828.60		35812[e]	
16b	455.7	446.6	448	a″
16a	556.2	572.0	563	a″
1	712.7	711.2	710	a′
11	756.1	788.3	790	a″
18a	912.3	910.8	900	a′
12	1003.2	994.6	1002	a′
18b	1151.3	1156.5	1150	a′
13	1252.5	1243.9	1250	a′
19a	1458.0	1424.8	1459	a′

[a]Ref. 20. [b]Measured in vacuum (cm^{-1}). [c]Multiplied by a scaling factor of 0.98. [d]Ref. 1. [e]Ref. 12.

It has been generally accepted that a calculation using the Gaussian 98 program at the DFT level with a 6-311g basis set effectively predicts vibrational mode frequencies within ± 10% of the experimental values. From the calculation of the *m*-tolunitrile, a total of 42 vibrational-mode frequencies were obtained, of which 28 and 14 vibrational modes belonged to 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 *o*-tolunitrile. Table 2 lists the vibrational mode frequencies of the *m*-tolunitrile in the ground electronic state as determined in this work, together with the symmetries of the vibrational modes.

The mode symmetry of *p*-isomers shows that the transition dipole moment is parallel to the 'a' or 'b' inertial axis for in-plane vibrations. Although the spectrum was observed with an excellent S/N, the bandshape could not easily be distinguished for the *m*- and *o*-isomers, since the transition dipole moment was of the hybrid-type. However, 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.[18] For the *m*-tolunitrile that also 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.

Several sequence bands of very weak intensity were observed in the vicinity of the very strong origin band at the approximate interval of 18.4, 38.8, 52.0, 101.1, and 125.7 cm^{-1} from the origin band, and are indicated by the Greek letters α, β, γ, δ, ε, and ξ respectively. Similar low frequency sequence bands were also observable in the vicinity of the strong vibronic band. 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, because the torsional frequencies observed in this work agree well with those reported from the *m*-tolunitrile in the ground electronic state.[12]

In summary, *m*-tolunitrile was vibronically excited using a technique of corona-excited supersonic expansion. The vibronic emission spectrum of the jet-cooled *m*-tolunitrile in the S$_1$ → 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 electronic transition and several vibrational mode frequencies in the ground electronic state were accurately obtained.

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