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Analysis of Rotationally Cooled Vibronic Emission Spectra ($1^2A_2 \rightarrow 1^2B_2$) of *m*-Xylyl Radical

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Received May 8, 1996

The rotationally cooled but electronically excited *m*-xylyl radical has been generated in a jet from the gas mixture of precursor *m*-xylene and buffer gas He by a technique of corona excited supersonic expansion. The visible vibronic emission spectra in the transition of $1^2A_2 \rightarrow 1^2B_2$ of *m*-xylyl radical in the gas phase have been recorded using a Fourier transform spectrometer. The spectra have been analyzed for the assignments of the vibrational frequencies in the electronic ground state with combination of the torsional frequencies reported previously.

Introduction

The vibronic structure and spectra of benzyl and three isomeric xylyl radicals have long been of interest to spectroscopists. They have been studied by a variety of techniques.¹ Substitution of a methyl group for a hydrogen in an aromatic compounds is supposed to have least perturbation on the aromatic ring. However, in the xylyl radicals, it is likely to have more significant effects. The small splitting between the *A* and *B* electronic states may be largely altered as well as the shift in the torsional and vibrational frequencies of the xylyl radicals. The information about the internal dynam-

ics of methyl groups may be provided by spectroscopic experiments at higher frequencies, in the visible and ultraviolet regions of the electromagnetic spectrum.^{2,3} This is because the properties of the potential energy surface along the methyl group torsional coordinate often change upon electronic excitation. A vibrationally resolved electronic spectrum may provide information about the difference in the barrier shape, height, or even conformational preference.

The xylyl radicals have been studied by numerous experimental and theoretical works. Most of earlier works on the xylyl radicals were limited to low resolution vibronic studies in either the gas phase⁴ or the solid phase.^{5,6} The earlier

works on the xylyl radical were reported by Schuler *et al.*⁷ and by Walker and Barrow⁸ in the visible region. Bindley *et al.*^{4,9} made tentative assignments of the vibronic bands from the emission spectra of xylyl radicals produced by an electric discharge of the corresponding xylenes. Leach *et al.*⁵ compared the ring vibrational modes and frequencies of the corresponding xylyl radicals with those of xylene species by employing a matrix isolation method. Also, Hiratsuka *et al.*¹⁰ identified the existence of the doublet states of the xylyl radicals which lie very closely to each other. Charlton and Thrush¹¹ measured the lifetime of radicals using a technique of laser induced fluorescence. The direction of the transition moment upon electronic excitation has been determined by Cossart-Magos *et al.*¹² from the rotational contour analysis of the emission spectra of the *o*-xylyl radical. Recently, Lin and Miller¹³ analyzed the methyl torsions of the xylyl radicals upon electronic excitation, in which they found a large phase shift in the torsional potential between the ground electronic state and the first excited electronic state of the *m*-xylyl radical. Also, Fukushima and Obi^{14,15} examined the vibronically coupling effect between two lowest excited electronic states of *p*-xylyl radical. Very recently, Selco and Carrick¹⁶ have reported the vibrational assignments with the torsional frequencies of the xylyl radicals.

In this study, we report the observation of visible vibronic emission spectra of the rotationally cooled but electronically excited *m*-xylyl radical and the analysis of the vibrational frequencies coupled with the torsional frequencies in the transition of $1^2A_2 \rightarrow 1^2B_2$.

Experimental Details

The experimental apparatus used for this work is very similar to those described previously.¹⁷⁻²¹ The *m*-xylyl radical was produced from the gas mixture of precursor *m*-xylene and buffer gas He by an electric dc discharge. The compound *m*-xylene of the spectroscopic grade was purchased commercially from Aldrich and used without further purification. The concentration of the parent compound in the gas mixture has been adjusted for the maximum fluorescence by opening the by-pass valve used for flowing the buffer gas and believed to be about 1%. Also, the pinhole nozzle which is similar to that developed by Engelking²² has been made by flame heating a 10 mm inner diameter and 3 mm thick walled quartz tube until one end was narrowed to the desired size opening. Of the several nozzles employed for this experiment, we have used the nozzle of 0.2 mm in orifice diameter for the final spectrum. For the corona discharge, the sharpened stainless steel rod of 2 mm in diameter and 30 cm in length has been inserted inside the nozzle for the anode and firmly fixed into the center of the nozzle by means of the teflon holder. The anode was connected to a 3.0 kV dc power supply via a 500 k Ω current limiting ballast resistor. Since the corona discharge of organic compounds produces messy materials such as carbon dust which easily block the pinhole of the nozzle and destabilize the discharge, the maximum integration time was limited by the stability of the discharge. The *m*-xylyl radical was formed in a green jet by flowing the gas mixture over an electric dc discharge between the anode and the pump which acts

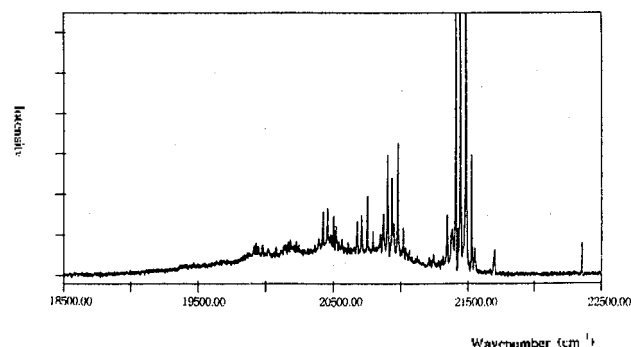


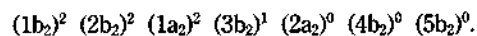
Figure 1. Rotationally cooled vibronic emission spectrum of the *m*-xylyl radical generated from the precursor *m*-xylene using a corona excited supersonic expansion. The band with the highest intensity at 21485.83 cm^{-1} is the origin band in the transition of $1^2A_2 \rightarrow 1^2B_2$.

as a cathode. The typical operating condition was 4-6 mA of discharge current at the 1000V dc potential. Also, the condition of electric discharge of *m*-xylene was optimized to produce the least amount of CH radical which emits very strong fluorescence of the $A^2\Delta \rightarrow X^2\Pi$ transition²³ in the visible region which overlaps with the vibronic emission spectrum of the *m*-xylyl radical in the transition of $1^2A_2 \rightarrow 1^2B_2$.

For the rotationally cooling, the backing pressure of about 2 atm has been combined with the chamber pressure of 1.0 Torr by using a mechanical rotary vacuum pump only. With this pressure difference, we have achieved the rotational temperature of 45 K which is good enough to resolve the vibronic bands in the spectrum.²⁴ Emission from the downstream jet of 5 mm below the nozzle was focussed onto the external port of the FT spectrometer (Bruker IFS-120HR). The instrument was operated with a Quartz-vis. beamsplitter, a home-made ac preamplifier, and the PMT (Hamamatsu model R106UH) detector for photon counter. For improvement of the signal to noise ratio of the spectrum, an optical color filter (Corning model No. 5-57) which has the spectral bandwidth of 18,500-31,500 cm^{-1} has been employed to block off the strong fluorescence from the buffer gas He. The spectral region from 16,000 to 33,000 cm^{-1} was scanned at the resolution of 2.0 cm^{-1} . A total of 250 scans have been added together over 30 min. to obtain the final spectrum shown in Figure 1. The accuracy of the frequency measurement is believed to be better than 0.01 cm^{-1} from the calibration with the I_2 transitions.²⁵

Results and Discussion

The *m*-xylyl radical has seven π delocalized electrons from the carbon atoms and thus has seven molecular orbitals (MOs) arising from the seven atomic orbitals (AOs). The seven MOs are represented by $1b_2$, $2b_2$, $1a_2$, $3b_2$, $2a_2$, $4b_2$, $5b_2$. According to the Hückel π electron theory, the $3b_2$ MO belongs to nonbonding, the three MO's ($1b_2$, $2b_2$, and $1a_2$) below $3b_2$ in energy are bonding and the higher ones ($2a_2$, $4b_2$, and $5b_2$) antibonding. Thus the electron configuration of the ground state (X^2B_2) is



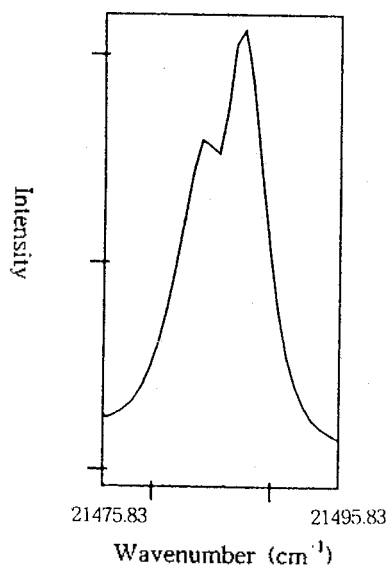


Figure 2. The bandshape of the origin band in the transition of $1^2A_2 \rightarrow 1^2B_2$ of the *m*-xylyl radical obtained at the low resolution.

For the lowest excited electronic states, there are two possible isoenergetic one electron promotions involving a_2 MOs, resulting in a degenerate pair of 2A_2 states. However, in the presence of configuration interaction (CI), the two degenerate pairs of zeroth order electronic states of the same symmetry interact and repel strongly, splitting widely the initially degenerate pairs. The lower part of the 2A_2 states, 1^2A_2 interacts vibronically with nearby 2^2B_2 electronic state.

Figure 1 shows a portion of the Fourier transform visible vibronic emission spectrum in the transition of $1^2A_2 \rightarrow 1^2B_2$ of *m*-xylyl radical in the gas phase. In the spectrum, most of the vibronic bands have been found in the frequency region of 19,000–22,000 cm^{-1} as other types of xylyl radicals.^{20,21} The origin band in the transition of $1^2A_2 \rightarrow 1^2B_2$ has been easily identified to locate at 21485.84 cm^{-1} which is in a good agreement with those reported previously.^{13,16} It is interesting to compare the position of the origin band of *m*-xylyl with that of isomers; 21345.00 and 21700.00 cm^{-1} for *o*-xylyl and *p*-xylyl radicals, respectively. Also, as expected, the origin band exhibits the strongest intensity. The vibronic emission spectrum of *m*-xylyl radical is seen to have the shortest frequency range compared to the other isomers.^{20,21} These shorter spectra imply that there is less structural change upon excitation in the meta isomer. Since the band origin has been calculated to locate between two branches of the typical bandshape²⁴ as shown in Figure 2, the frequency of the each band has been measured at the minimum intensity between two branches. The measured frequencies, the relative intensity with respect to those of the origin band, and the assignments of the vibronic bands observed are listed in Table 1.

From the assignment of the vibrational modes, no hot vibronic band has been observed from the observed spectra, even though the *m*-xylyl radical has been generated by the method of high voltage electric dc discharge which is generally known to produce vibrationally hot molecules.²⁶ We believe the reason for the cold vibrational phenomenon in the

Table 1. Observed Band Positions of Jet Cooled *m*-Xylyl Radical in the Gas Phase^a

Position	Relative Intensity ^b	Spacing from the Origin ^c	Assignments ^d
21700.00	5.85	-214.17	<i>p</i> -xylyl origin
21672.08	1.47	-186.25	
21663.33	1.18	-177.50	
21623.75	1.20	-137.92	$\tau'(3) \equiv 5e-1e$
21585.94	1.42	-100.11	
21551.98	6.39	-66.15	$\tau'(2) \equiv 3a_1/3a_2-0a_1$
21527.50	27.93	-41.67	$\tau'(1) \equiv 2e-1e$
21485.83	100.00	0.00	0_0^0
21442.60	85.00	43.23	$\tau(1) \equiv 1e-2e$
21426.67	10.85	59.16	$\tau(2) \equiv 2e-4e$
21410.70	66.70	75.13	$\tau(3) \equiv 0a_1-3a_1/3a_2$
21383.33	10.76	102.50	$\tau(4) \equiv 1e-4e, 2e-5e, \text{benzyl origin}$
21373.10	9.62	112.73	
21345.26	14.15	140.57	$\tau(5) \equiv 1e-5e, \text{o-xylyl origin}$
21313.44	4.56	172.39	$16b_1^0$ of <i>p</i> -xylyl
21298.13	3.62	187.71	
21279.87	3.58	205.96	$\tau(6) \equiv 0a_1-6a_1$
21241.54	4.55	243.30	$6a_1^0$ of <i>p</i> -xylyl
21210.74	4.25	275.09	
21123.51	4.54	362.32	
21110.38	4.49	375.45	$16_1^0 + \tau'(1)$
21062.13	5.25	423.70	$16_1^0, 6b_1^0$ of <i>p</i> -xylyl
21036.46	6.61	449.37	
21019.10	11.23	466.73	$16_1^0 + \tau(1)$
21003.01	5.98	482.82	$16_1^0 + \tau(2)$
20978.96	30.85	506.87	$6b_1^0$
20973.72	23.59	512.11	$6b_1^0 + 2e-2e$
20947.34	11.13	538.49	$6a_1^0$
20934.05	21.42	551.78	$6b_1^0 + \tau(1), 16a_1^0$ of <i>o</i> -xylyl
20927.47	7.19	558.36	$16_1^0 + \tau'(3)$
20917.89	7.83	567.94	$6b_1^0 + \tau(2)$
20901.89	28.02	583.94	$6a_1^0 + \tau(1), 6b_1^0 + \tau(3)$
20871.43	14.43	614.40	$6a_1^0 + \tau(3), 1_1^0$ of <i>p</i> -xylyl
20846.25	8.61	639.58	$6a_1^0 + \tau(4), 6b_1^0$ of <i>o</i> -xylyl
20815.97	6.82	669.86	
20793.46	10.28	692.37	
20763.20	6.66	722.63	$10_1^0 + \tau'(1), 6a_1^0$ of <i>o</i> -xylyl
20751.92	18.49	733.91	12_1^0
20708.17	14.06	777.66	$10_1^0, 12_1^0 + \tau(1)$
20681.43	7.49	804.40	$12_1^0 + \tau(3)$
20676.37	12.74	809.46	$17b_1^0 + \tau'(2)$
20653.86	6.77	831.97	$17b_1^0 + \tau'(1)$
20644.06	6.35	841.78	$12_1^0 + \tau(4)$
20628.60	6.42	857.23	
20609.07	7.20	876.76	$17b_1^0, 1_1^0$ of <i>o</i> -xylyl
20585.95	6.73	899.88	
20563.26	7.29	922.57	$17b_1^0 + (1)$
20541.83	8.11	944.00	$1_1^0 + \tau'(1)$
20521.24	11.51	964.59	5_1^0
20502.44	13.77	983.39	$1_1^0, 10_1^0 + \tau(6)$
20479.25	9.62	1006.58	$5_1^0 + \tau(1)$

Table 1. Continued

Position	Relative Intensity ^b	Spacing from the Origin ^c	Assignments ^d
20456.88	15.47	1028.95	1 ₁ ⁰ +τ(1)
20445.23	7.85	1040.60	5 ₁ ⁰ +τ(3)
20423.93	14.81	1061.90	1 ₁ ⁰ +τ(3)
20391.43	8.69	1094.40	18a ₁ ⁰
20362.46	7.21	1123.37	1 ₁ ⁰ +τ(5)
20329.91	6.36	1155.92	1 ₁ ⁰ +τ(3)
20311.54	6.36	1174.29	18a ₁ ⁰ +τ(3)
20284.92	6.20	1200.91	
20268.77	6.08	1217.06	14 ₁ ⁰ +τ'(1)
20245.66	7.19	1240.17	13 ₁ ⁰ , 6b ₁ ⁰ , 12 ₁ ⁰
20227.95	8.08	1257.88	14 ₁ ⁰
20212.77	7.21	1273.06	6a ₁ ⁰ , 12 ₁ ⁰
20183.13	8.36	1302.70	14 ₁ ⁰ +τ(1)
20166.81	8.00	1319.02	14 ₁ ⁰ +τ(2)
20150.90	7.21	1334.93	14 ₁ ⁰ +τ(3)
20142.11	6.83	1343.72	13 ₁ ⁰ +τ(4)
20133.57	7.03	1352.26	6b ₁ ⁰ , 10 ₁ ⁰ +τ(3)
20132.61	7.01	1353.22	6a ₁ ⁰ , 12 ₁ ⁰ +τ(3)
20019.32	6.33	1466.51	19b ₁ ⁰ +τ'(1)
19977.02	7.19	1508.81	8a ₁ ⁰ +τ'(2)
19975.58	7.16	1510.25	19b ₁ ⁰
19946.26	6.83	1539.57	8b ₁ ⁰
19931.46	7.61	1554.37	19b ₁ ⁰ +τ(1)
19916.98	7.08	1568.85	19b ₁ ⁰ +τ(2)
19915.48	7.09	1570.35	8a ₁ ⁰
19878.66	5.38	1607.17	8b ₁ ⁰ +τ(3)
19867.07	5.42	1618.76	8a ₁ ⁰ +τ(1)

^ain units of cm⁻¹. ^bdetermined from the comparison with the origin band. ^cmeasured in cm⁻¹ from the origin band at 21485.83 cm⁻¹. ^dWilson's notation in Ref. (33).

excited state is due to the design of the nozzle and the position of the electrode inside the pinhole. Since the discharge occurs at the relatively high pressure region in this system, molecules initially excited to the many higher vibrational states undergo collisional relaxation to the ground vibrational state of the first excited electronic state by collision with He before they emit.

In addition to the origin band, we have observed many vibronic modes. The modes assigned in the electronic ground state from the spectra are as follows: 1 (ring breath, 983.39 cm⁻¹), 5 (CH bend 964.59 cm⁻¹), 6a (ring deformation, 538.49 cm⁻¹), 6b (ring deformation, 506.87 cm⁻¹), 8a (ring stretch, 1570.35 cm⁻¹), 8b (ring stretch, 1539.57 cm⁻¹), 10a (CH out-of-plane, 777.66 cm⁻¹), 12 (ring deformation, 733.91 cm⁻¹), 13 (CH stretch, 1240.17 cm⁻¹), 14 (CH stretch 1257.88 cm⁻¹), 16a (ring deformation, 423.70 cm⁻¹), 17b (CH out-of-plane, 876.76 cm⁻¹), 18a (CH bend, 1094.40 cm⁻¹), 19b (ring stretch and deformation, 1510.25 cm⁻¹).

For each mode, we have found several low frequency torsional transitions which are also listed in Table 1. A change in the conformation of a methyl group manifests itself in an electronic emission spectrum as a progression of vibronic

Table 2. Vibrational Frequencies of *m*-Xylyl Radical in the Gas Phase^a

Vibrational Mode ^b	This Work	Previous Work ^c	<i>m</i> -Xylene ^d
1	983.39	983.5	723
2			3052
3			1264
4			695
5	964.59	968	965
6a	538.49	529.4	535
6b	506.87	513.5	515
7a			
7b			903
8a	1570.35	1570.4	1595
8b	1539.57	1539.1	1615
9a			299
9b			1167
10a	777.66	768	227
10b			206
11			766
12	733.91	732.6	1003
13	1240.17	1253.1	1252
14	1257.88	1267.1	1303
15			404
16a	423.70	423.3	483
16b			431
17a			892
17b	876.76	876	874
18a	1094.40	1096.8	1092
18b			1125
19a			1460
19b	1510.25	1511.2	1492
20a			3030
20b			3082

^ain units of cm⁻¹. ^bref. (33). ^cref. (16). ^dref. (34).

bands in the torsional mode in accord with the Franck-Condon principle. The presence of low frequency bands as progressions built on the origin and the vibronic bands indicates that there is a significant change in the torsional potential of the methyl group in the ground state compared with the excited electronic state. The potential energy function that describes the motion of the methyl group may not be the same in the different electronic states of the molecule. There may be a difference in the barrier shape, height, or even conformational preference. For *m*-xylyl radical which contains a single methyl rotor, G₆ permutation inversion symmetry group is appropriate because the frame to which the methyl group is attached has no symmetry about the torsional axis. In this symmetry group, $m=0, +3n, m=-3n$, and $m \neq 0, \pm 3$ torsional levels have different symmetries, A₁, A₂, and E, respectively. For the transition between torsional levels, a rigorous A \leftrightarrow A and E \leftrightarrow E selection rule can be applied to in electronic spectra. Also, even under the most extreme expansion conditions, both the A and E ground state levels are populated and both A \leftrightarrow A and E \leftrightarrow E transitions are observed in fluorescence excitation spectra. The bands obser-

ved at low frequency shift from the origin band matches the values for torsional frequencies previously given by Lin and Miller.¹³

From Table 1, the spectrum of *m*-xylyl radical exhibits bands attributable to the other isomers, the *m*-xylyl radical, *o*-xylyl radical and even benzyl radical even though we have employed a highly pure sample of *m*-xylene. The observation of other types of xylyl radicals in the emission spectra agrees with those reported by Selco and Carrick.¹⁶ The amounts of benzyl, *o*-xylyl, and *p*-xylyl radicals produced are small relative to the total amount of *m*-xylyl radical. The intensity of all other radicals except for *m*-xylyl radical is comparable to each other. Thus, it can be deduced that the xylyl radical can be generated via a benzovalene or prismane like intermediate or migration of a methyl group.²⁷⁻³⁰

From the assignment of the bands, it is very useful to tabulate in the Table 2 the gas phase frequencies of the normal modes of vibration of the *m*-xylyl radical in the ground electronic state. From the comparison of the vibrational frequencies in Table 2, it is clearly seen that most of the frequencies determined in this work are in good agreements with those previously obtained.¹⁶ There are a few combination bands coupled with 6a or 6b in the *m*-xylyl radical. From the comparison of the vibrational frequencies of *m*-xylyl radical with those of the corresponding xylene, we have concluded that the isodynamic molecular approximation^{31,32} can be applied to the vibration of the *m*-xylyl radical.

Although the calculation of Hiratsuka *et al.*¹⁰ and Branciard-Larcher³¹ predicts the existence of the second electronically excited state (2^2B_2) above 600 cm^{-1} above the 1^2A_2 state, we have found no evidence of this second excited state which are consistent with those reported.^{13,16}

Summary

Rotationally cooled but electronically excited *m*-xylyl radical has been generated in a jet by a method of corona excited supersonic expansion. The vibronic emission spectrum in the transition of $1^2A_2 \rightarrow 1^2B_2$ was obtained with a Fourier transform spectrometer in the visible frequency region. The bands observed in this spectrum have been assigned according to the vibrational and torsional frequencies. The more accurate vibrational frequencies have been obtained for the vibrational modes in the electronic ground state of the *m*-xylyl radical. From the assignments, we have confirmed the previous observation for the generation of the other isomers upon excitation. Even though we have used the electric discharge method for the generation and excitation of the *m*-xylyl, no hot vibronic band has been observed. We believe that the collisional relaxation process of the *m*-xylyl radical is very efficient in the nozzle system employed for this study.

Acknowledgment. The present study has been supported by the Korea Research Foundation through Non-Direct Research Fund. The authors thank the Ohio State University for allowance to use the FT-spectrometer (Bruker IFS-120 HR).

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