

Rotationally Cooled Emission Spectra of *p*-Xylyl Radical

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The *p*-xylyl radical has been produced in a jet from the precursor *p*-xylene with a corona excited supersonic expansion. Rotationally cooled vibronic emission spectra in the transition of $1^2A_2 \rightarrow 1^2B_2$ of the *p*-xylyl radical have been recorded using a Fourier transform spectrometer. The spectra were analyzed on the basis of the known vibrational frequencies and the bandshapes given by the rotational selection rules.

Introduction

While the benzyl radical has received much attention as a representative of aromatic free radicals,¹⁻⁵ alkyl substituted benzyl (xylyl) radicals^{6,7} have been less studied as large aromatic radicals. The earlier works of the xylyl radical were reported by Schuler *et al.*⁸ and by Walker and Barrow⁹ in the visible region. Bindley *et al.*^{10,11} made tentative assignments of the vibronic bands from the analysis of emission spectra of xylyl radicals produced by an electric discharge of the corresponding xylenes. Leach *et al.*¹² 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.*¹³ have theoretically predicted the existence of the doublet states of the xylyl radicals which lie very closely to each other. Charlton and Thrush¹⁴ measured the lifetime of radicals using a technique of laser induced fluorescence. Most of earlier works on the xylyl radicals are limited to low resolution vibronic studies in either the gas phase¹⁰ or the solid phase.^{12,15}

Cossart-Magos *et al.*⁶ have tried to identify without the explicit conclusion the symmetry of the vibronic bands, particularly the modes 6a and 6b from the emission spectra. Recently, Lin and Miller^{2,16} have employed the technique of laser induced fluorescence to identify the torsional effect in xylyl radicals. Very recently, Selco and Carrick¹⁷ have presented the analysis of low resolution vibronic emission spectra of *p*-xylyl radical obtained by using a technique of corona excited supersonic expansion.

With high resolution work, Cossart-Magos *et al.*⁶ have tried to determine the structure of *p*-xylyl radical by comparing the rotational contours of the vibronic band observed with those calculated. Recently, Miller group has given the quantitative analysis of the high resolution LIF spectra of *p*-xylyl radical for accurate rotational constants and torsional barrier heights.²

In this paper, we describe the observation and the analysis of the visible vibronic emission spectra in the transition of $1^2A_2 \rightarrow 1^2B_2$ of *p*-xylyl radical which was generated in a jet with a corona excited supersonic expansion.

Experimental Details

The experimental details for the observation of rotationally cooled emission spectra of *p*-xylyl radical are very similar to those described previously.¹⁸⁻²¹ The gas mixture of *p*-xy-

lene and an inert buffer gas He was used for the generation of the *p*-xylyl radical. The compound *p*-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 by immersing the sample chamber in a temperature controllable water bath for the maximum fluorescence and believed to be about 1%.

Since the spectra of *p*-xylyl radical obtained without cooling exhibit a characteristic of almost entirely diffuse,⁶ the rotational cooling has been employed using a technique of supersonic expansion. The 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 glass tube until one end was narrowed to the desired size opening. Of the several nozzles made in this method, we have employed the nozzle of 0.2 mm in diameter which has been proven to be the most effective for this experiment. For the corona discharge, the sharpened stainless steel anode of 2 mm in diameter and 30 cm in length has been inserted inside the nozzle for an anode and firmly fixed into the center of the nozzle by means of the teflon holder. The anode was connected to a 3 kV dc power supply via a 500 k Ω current limiting ballast resistor. Since the corona discharge of organic compounds produces messy materials which stick to on the surface of nozzle and quickly destroy the stability of the discharge, the discharge occurs at the low pressure region by placing the tip of the anode outward the pinhole. The *p*-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 as the cathode. The typical operating condition was 4-6 mA discharge current at the 1000 V dc potential. Also, the condition of electric discharge of *p*-xylene was also optimized to produce the least amount of CH radical which emits very strong fluorescence in the visible region. For this spectrum, the current and voltage of the discharge have been adjusted to minimize the production of the CH radical of which strong emission bands of the $A^2\Delta \rightarrow X^2\Pi$ transition²³ overlap with those of the *p*-xylyl radical.

For the rotationally cooling, the backing pressure of the nozzle has been measured to be about 2 atm. The pressure in the expansion chamber during the operation was maintained to be lower than 1.0 Torr by using the mechanical vacuum pump only. With this difference in pressure, we have obtained the rotational temperature of 45 K which is enough

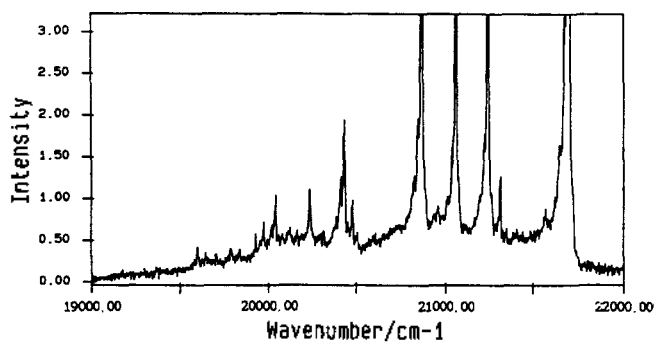


Figure 1. Rotationally cooled vibronic emission spectrum of the *p*-xylyl radical generated using a corona excited supersonic expansion of *p*-xylene. The band with the highest intensity at 21700.00 cm^{-1} is the origin band of the transition of $1^2A_2 \rightarrow 1^2B_2$.

to resolve the vibronic bands in this spectrum. A jet area of 2 mm in diameter below the nozzle orifice 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 the improvement of signal to noise ratio of the spectrum, an optical color filter (Corning model No. 5-57) of the spectral bandwidth of 18,500-31,500 cm^{-1} has been used to block off the strong fluorescence from the carrier 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 10 min. to obtain the final spectrum shown in Figure 1. The accuracy of the frequency is believed to be better than 0.01 cm^{-1} at this resolution from the calibration with the I_2 transitions.²⁴

Results and Discussion

The rotationally cooled vibronic emission spectra of *p*-xylyl radical in the transition of $1^2A_2 \rightarrow 1^2B_2$ is shown in Figure 1. Of the spectral region scanned, 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. Even though the bandwidth has been narrowed by a rotational cooling, it shows a little bit wider than that of *o*-xylyl due to the existence of 2 nearby torsional levels and almost free internal rotation of methyl group. The rotational temperature of the vibronic bands in the spectrum is believed to be about 45 K from the simulation to the rotational contours of the vibronic bands in the benzyl spectrum which has been obtained under the similar experimental conditions.²⁵

Since, according to the simulated spectrum of the *p*-xylyl,⁶ the band origin of the vibronic band was located at the position of minimum intensity, the accurate frequency of the vibronic bands has been determined by measuring the position of minimum intensity between two branches. The frequency of the origin band in the transition of $1^2A_2 \rightarrow 1^2B_2$ has been measured to be 21700.00 cm^{-1} which is in a good agreement with those reported previously.^{6,17} The peak of maximum intensity is considered to arise from R sub-branches of low K_a .

The measured frequencies, the relative intensity, and the

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

Positions ^a	Relative intensity ^b	Spacing from the origin ^c	Assignments
21700.00	100	0.00	0_0^0
21680.00	28.42	20.42	$1e'' \rightarrow 2e' \equiv \tau(2)$
21676.51	28.50	23.49	$11_1^1, 3a_1'' \rightarrow 0a_1' \equiv \tau(3)$
21661.56	13.42	38.44	$\alpha = 38.44$
21656.09	13.75	43.91	$3a_1'' \rightarrow 3a_2'' \equiv \tau(4)$
21654.61	13.75	45.39	
21648.91	13.75	51.09	$0a_1' \rightarrow 3a_1'' \equiv \tau(5)$
21622.89	8.58	77.11	$10b_1^1, 1e'' \rightarrow 4e' \equiv \tau(6)$
21604.69	6.55	95.31	
21587.81	6.41	112.19	
21568.83	7.46	131.17	$1e'' \rightarrow 5e'' \equiv \tau(7)$
21542.50	5.35	157.50	
21525.78	5.35	174.22	$6a_2' \rightarrow 0a_1' \equiv \tau(8)$
21507.97	5.24	192.03	$0a_1' \rightarrow 6a_1' / 6a_2' \equiv \tau(9)$
21485.63	5.21	214.38	<i>m</i> -xylyl origin
21443.59	5.12	256.41	$1e'' \rightarrow 7e'' \equiv \tau(10)$
21384.69	5.04	315.31	benzyl
21344.53	5.45	355.47	<i>o</i> -xylyl origin
21311.52	10.58	388.48	$16b_1^0$
21285.27	5.93	414.73	
21241.50	42.25	458.50	$6a_1^0$
21218.98	14.92	481.02	$6a_1^0 - 12_1^0 + 16b_2^0$
21213.05	13.33	486.95	
21203.48	9.00	496.52	$6a_1^0 + \alpha$
21193.09	8.75	506.91	$6a_1^0 + \tau(5)$
21163.40	6.58	535.62	$6a_1^0 + \tau(6)$
21063.17	48.67	636.83	$6b_1^0$
21036.21	13.50	663.79	
21024.34	8.67	675.66	$6b_1^0 + \alpha$
21021.60	8.75	678.40	
21010.51	8.17	689.49	$* = 689.49$
20955.58	7.73	744.42	12_1^0
20933.09	6.90	766.91	$6b_1^0 + \tau(7) \quad 16b_2^0$
20869.17	47.50	830.83	1_1^0
20850.27	16.42	849.73	
20846.76	16.50	853.24	$1_1^0 + \tau(3) \quad (6b_1^0 \text{ } o\text{-xylyl})$
20828.20	10.67	871.80	$1_1^0 + \tau(4)$
20783.98	6.61	916.02	
20598.75	4.75	1101.25	$15_1^0, 18b_1^0$
20494.10	4.68	1205.90	$18a_1^0$
20477.46	8.31	1222.54	$7a_1^0$
20450.74	6.11	1249.26	13_1^0
20431.91	1.63	1268.09	$6b_2^0$
20410.98	10.58	1289.02	$6b_2^0 + \tau(3)$
20386.99	6.60	1313.01	3_1^0
20317.07	5.05	1382.93	
20234.41	9.33	1465.59	$12_2^0, 6b_1^0 + 1_1^0$
20162.89	5.23	1537.11	$19a_1^0$
20123.44	5.43	1576.56	$8b_1^0$
20080.00	4.73	1620.00	
20053.91	4.77	1646.09	1_2^0
20039.69	8.75	1660.31	$8a_1^0$

20020.23	5.78	1679.77	$8a_1^0 + \tau(3)$
19997.97	4.32	1702.03	
19974.92	6.08	1725.08	$6b_1^0 + 15_1^0$
19955.86	4.21	1744.14	
19839.92	3.36	1860.08	$16b_2^0 + 15_1^0$
19794.06	3.41	1905.94	$* + 7a_1^0$
19707.66	2.90	1992.34	$12_1^0 + 6b_2^0$
19650.27	3.03	2049.73	
19602.77	3.56	2097.23	$6a_1^0 + 8a_1^0$

^aIn units of cm^{-1} . ^bDetermined from the comparison with the origin band. ^cMeasured in cm^{-1} from the origin band at 21700.00 cm^{-1} .

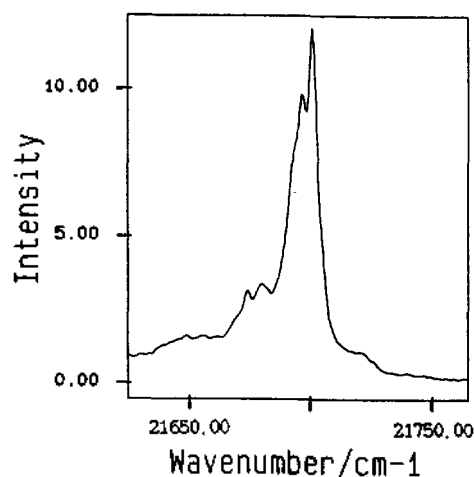


Figure 2. The bandshape of the origin band at 21700.00 cm^{-1} . The symmetry of the origin band in the transition of $1^2A_2 \rightarrow 1^2B_2$ of *p*-xylyl radical belongs to the type B because the electric transition moment is parallel to the *b* axis.

assignments of the vibronic bands observed are listed in Table 1. The measured intensity of each vibronic band has been normalized with that of the origin band. The assignments of the vibronic bands observed has been carried out by means of not only the bandshape analysis but also the known vibrational frequencies.¹²

The bandshape is strongly dependent on the same parameters one would obtain from a completely resolved spectrum, that is, the rotational selection rules, the rotational temperature, and the rotational constants at both the ground and the excited electronic states. Also, it has been well known that the bandshape is much more sensitive to the changes of rotational constants during the transition rather than to the absolute values of the constants. For the case of *p*-xylyl radical, the vibronic bands are clearly of type B or type A since the transition moment lying in the molecular plane is parallel to the '*b*' axis or the '*a*' axis.⁶ Moreover, the symmetry of the origin band in the transition of $1^2A_2 \rightarrow 1^2B_2$ of *p*-xylyl radical belongs to the type B because the electric transition moment is parallel to the '*b*' axis.²⁶ The bandshape of the origin band is clearly seen in Figure 2.

It has been mentioned that the benzene's two degenerate node 6 splits into $6a$ and $6b$ in the case of benzyl and xylyl radicals. Also, there have been reported that the vibronic

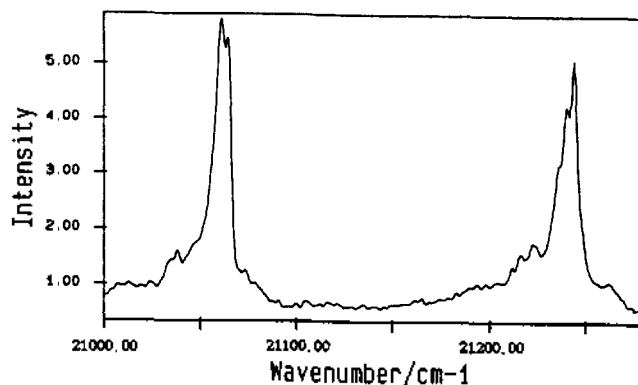


Figure 3. Comparison of the bandshapes between two vibronic bands. The band at 21063.17 cm^{-1} is from $6b_1^0$, while that at 21241.50 cm^{-1} is from $6a_1^0$ which shows almost same bandshape as the origin band shown in Figure 2.

bands $6a_1^0$ and $6b_1^0$ exhibit the strongest intensity in the emission spectra of the benzyl and xylyl radicals.^{1,21} As for the symmetry of the transitions, the band $6a_1^0$ have same symmetry of the type B as the origin band 0_0^0 , while the band $6b_1^0$ belongs to the type A from the theoretical analysis of the vibrational modes of *p*-xylyl radical.²⁷

From the analysis of the bandshapes of vibronic bands in the emission spectra, Cossart-Magos and Cossart⁶ have interpreted the bands at -457.0 cm^{-1} and -636.7 cm^{-1} to be $6b_1^0$ and $6a_1^0$, respectively. But, as they have pointed out, the assignments were not very clear due to the weak S/N of the spectra. Very recently, Selco and Carrick also have given the confirmation of the assignment of Cossart-Magos and Cossart. On the other hand, from the analysis of the dispersed fluorescence spectra of jet cooled *p*-xylyl, Fukushima and Obi³ have determined the frequencies of the vibrational modes $6a$ and $6b$ in the ground state to be 450 and 630 cm^{-1} , respectively, which are contrary to the results given by the emission spectra.^{6,17} However, it was not possible to identify the symmetry of the bands because of the limited resolution in the dispersed fluorescence spectra. Thus, it is necessary to identify the symmetry of the vibronic bands $6a_1^0$ and $6b_1^0$ using the spectrum of better resolution.

The bandshape of the bands $6a_1^0$ and $6b_1^0$ is shown in Figure 3. From the comparison with the bandshape in Figure 2, it is clear that the peak at 21241.50 cm^{-1} has the same bandshape as that of the origin band, while the peak at 21063.17 cm^{-1} shows different bandshape from the origin band. Thus, we can easily determine the bands at 21241.50 cm^{-1} and at 21063.17 cm^{-1} to be the $6a_1^0$ and the $6b_1^0$, respectively.

In addition to the assignment of $6a$ (ring deformation) and $6b$ (ring deformation), we have found many vibrational structures; the mode 1 (ring breath, 830.83 cm^{-1}), 3 (CH bend, 1313.01 cm^{-1}), 7a (CH stretch, 1224.54 cm^{-1}), 8a (ring stretch, 1660.31 cm^{-1}), 8b (ring stretch, 1576.56 cm^{-1}), 12 (ring deformation, 744.42 cm^{-1}), 13 (CH stretch, 1249.26 cm^{-1}), 15 (CH stretch, 1101.25 cm^{-1}), 16 (ring deformation, 388.48 cm^{-1}), 18a (CH bend, 1205.90 cm^{-1}), 18b (CH bend, 1101.25 cm^{-1}), 19a (ring stretch and deformation, 1537.11 cm^{-1}). For these modes, we have found several progressions and combinations of the normal modes of vibration, as shown in Table

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

Vibrational Mode	This Work	Previous Work ^b	<i>p</i> -Xylene ^c
1	830.83	826	826
2			3054
3	1313.01		1313
4			702
5			934
6a	458.50	451	459
6b	636.83	640.7	645
7a	1222.54	1219	1205
7b			3030
8a	1660.31	1664	1618
8b	1576.56	1573	1581
9a			1183
9b			386
10a			810
10b			313
11			170
12	744.42	736	671
13	1249.26		1248
14			1324
15	1101.25	1123	292
16a			410
16b	388.48	389	483
17a			962
17b			795
18a	1205.90		1024
18b	1101.25		1100
19a	1537.11	1500	1529
19b			1421
20a			3095
20b			3017

^aIn units of cm⁻¹. ^bRef. (12). ^cRef. (30).

1. In this study, however, it is not possible to assign all of the bands observed since there are numerous ways of combinations.

From the assignment of the bands, it is very useful to tabulate in the Table 2 the frequencies of the normal modes of vibration of the *p*-xylyl radical in the gas phase. 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 obtained using the matrix isolation method.¹²

As for the benzene derivatives, it has been suggested that the isodynamic molecular approximation^{28,29} be very useful for the estimation of the vibrational frequencies of the corresponding radicals. From the comparison of the vibrational frequencies of the *p*-xylyl radical with those³⁰ of the *p*-xylene in Table 2, we have concluded that the isodynamic molecular approximation can be applied to the vibration of the *p*-xylyl radical.

From Table 1, there appear to be peaks in the spectrum attributable to the benzyl, *o*-xylyl and *m*-xylyl radicals, even

though we have employed a highly pure sample of *p*-xylene. Thus, it can be deduced that the production of xylyl radical can be generated via a benzvalence or prismane type intermediate.³¹⁻³⁴ The observation of other types of xylyl radicals in the emission spectra agrees with those reported by Selco and Carrick.¹⁷ The amounts of benzyl, *m*-xylyl, and *o*-xylyl radicals produced are small relative to the total amount of *p*-xylyl radical. The intensity of all other radicals except for *p*-xylyl radical is comparable to each other.

The band observed at low frequency shift from the origin band matches the values for torsional frequencies previously observed/calculated by Lin and Miller.¹⁶

Although the calculation of Hiratsuka *et al.*¹³ and Branciard-Larcher³⁵ predicts the existence of the second electronically excited state (2^2B_2) above 600 cm⁻¹ above the 1^2A_2 state, we find no evidence of this second excited state which are consistent with those reported.^{16,17}

Summary

In this study, rotationally cooled but vibronic excited *p*-xylyl radicals have been produced in a jet from *p*-xylene using a technique of corona excited supersonic expansion. The emission spectra of *p*-xylyl in the transition of $1^2A \rightarrow 1^2B_2$ has been obtained using a Fourier transform spectrometer. From the analysis of the bandshapes, we have determined the assignments of the bands $6a_1^0$ and $6b_1^0$. In addition, the assignment of many vibronic transitions has been carried out for the accurate vibrational frequencies in the ground state. Also, we have identified the generation of the benzyl, *o*-xylyl and *m*-xylyl radicals from the electric discharge of *p*-xylene, which could explain the mechanism for the molecular rearrangement during the corona discharge. Finally, we have confirmed the torsional levels given by Lin and Miller.¹⁶

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Studies on the Formation of Poly(ethylene 2,6-naphthalate). 1. Polycondensation Catalyzed by Various Metal Compounds

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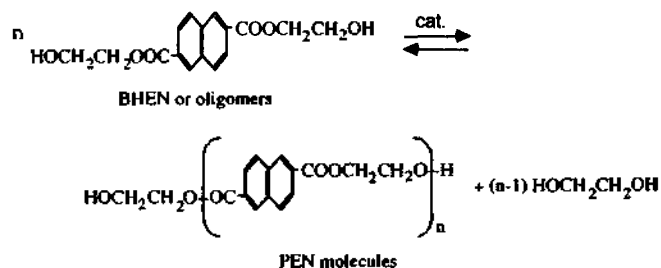
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The polycondensations of bis(2-hydroxyethyl) naphthalate were kinetically investigated in the presence of various metallic compounds as catalysts at 295 °C. The effect of the catalyst nature in the polycondensation has been studied. The order of catalytic activity on the formation of poly(ethylene 2,6-naphthalate) was found to be related to the stability constants which are indicated in an index of the catalytic activity.

Introduction

The information concerning the role of the metal compounds as catalysts in the poly(ethylene 2,6-naphthalate) (PEN)¹⁻³ polymerization is very important to understand the catalytic activity.

The synthesis of PEN polymer is carried out in a two step process; that is, transesterification and polycondensation reaction. In the first step, dimethyl 2,6-naphthalate (DMN) reacts with ethylene glycol forming methanol and bis(2-hydroxyethyl) naphthalate (BHEN) oligomer. In the second step, the BHEN oligomer is converted to high molecular weight PEN polymer by elimination of glycol between the hydroxyethyl ester end groups. In both reaction, various metallic compounds are used as the catalyst;



In general, the polycondensation of BHEN is subjected to temperatures from 285 to 300 °C. The rate of the propagation and degradation under these conditions depends largely upon the reaction temperature as well as on the kind and amount of metal compounds used as polycondensation catalysts.

The mechanism by which metal compounds act as poly-

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