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Visible Emission Spectra of *o*-Xylyl Radical

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The visible emission spectra of the *o*-xylyl radical in the gas phase have been obtained using a Fourier transform spectrometer coupled with a technique of supersonic expansion. The *o*-xylyl radical was generated in a jet by expansion with an inert buffer gas He from a high voltage dc discharge of the precursor *o*-xylene. The spectra were analyzed on the basis of the rotational contours of the vibronic bands as well as the known vibrational frequencies by a matrix isolation method.

Introduction

Alkyl substituted benzyl radicals[1,2] have less studied as large aromatic radicals, while much attention has been given on the vibronic structure of benzyl radical as a representative of aromatic free radicals.[3~7] The earlier works of the xylyl radical was reported by Schuler *et al.*[8] and by Walker and Barrow[9] in the visible region. Bindley *et al.*[10,11] made tentative assignments of the vibronic bands from the visible emission spectra of xylyl radicals generated by an electric discharge of the corresponding xylenes and alkyl substituted toluene. Leach *et al.*[12] compared the ring vibrational modes and frequencies of the corresponding xylyl radicals with those of xylene species using a matrix isolation method. The existence of the doublet states of the xylyl radicals which lie very closely to each other was identified by Hiratsuka *et al.*[13] Charlton and Thrush[14] measured the lifetime of radicals using a technique of laser induced fluorescence. Most of earlier works on *o*-xylyl radical are limited to low resolution studies of the vibrational structure of the gas phase[10] and the solid solution emission.[12,15] For high resolution work, Cossart-Magos *et al.*[1] extended the rotational contour analysis of benzyl radical to that of the *o*-xylyl. From the comparison of calculated with observed spectra, they have determined the direction of the dipole moment of the molecule upon the electronic excitation. Also, there has been suggested that the strength of the electronic interaction between the methyl group and the benzene ring be undoubtedly the second order in *o*-xylyl as compared to the interaction between the methylene group and the ring. Thus, the electronic states of the *o*-xylyl radical should exhibit a close relation to those of the benzyl radical. The identification of the electronic states was carried out by Cossart-Magos *et al.*[1] who concluded that the lowest excited electronic state of *o*-xylyl radical is of $^2A_2$ symmetry from which the two lowest excited electronic states are similar to those of the parental benzyl 1^2A_2 and 2^2B_2 states. As shown by Selco and Carrick recently,[3,7] the accurate frequencies of vibronic bands in emission could be determined from the rotationally cooled but vibronically hot spectra.

In this study, we describe the observation and the analysis of the vibronic bands of the visible electronic emission spectra of *o*-xylyl radical in the gas phase.

Experimental Details

The observation of low resolution visible emission spectra of *o*-xylyl radical has been performed using the experimental setup similar to those described previously.[16~18] The parent compound *o*-xylene of the spectroscopic grade was purchased commercially from Aldrich and used without further purification. The vapors of the compound were expanded with an inert carrier gas He through 0.2 mm diameter of quartz nozzle into the vacuum chamber made by a six-way cross Pyrex glass tube of 5.0 cm in diameter. The concentration of the parent compound in a carrier gas could be controlled by immersing the sample in a temperature-controllable water bath or by adjusting the opening of the bypass valve of the carrier gas. In this experiment, the concentration of the precursor was adjusted for the maximum fluorescence and believed to be about 1% in the gas mixture.

For the nozzle which is similar to that developed by Engelking,[19] a 3 mm thick walled glass tube was flame heated until one end was narrowed to the desired size opening. The *o*-xylyl radical was formed in a green jet by flowing the gas mixture over an electric dc discharge between the anode fixed inside the nozzle and the pump which acts as the cathode. The sharpened stainless steel anode of 2 mm in diameter was connected to a 3000 V dc power supply *via* a 500 KΩ current limiting ballast resister. The condition

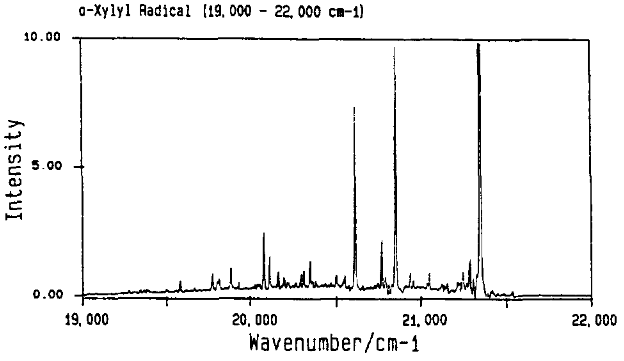

Figure 1. Low resolution visible emission spectra of the *o*-xylyl radical generated by an electric dc discharge of *o*-xylene. The most intensive peak is the band located at 21,348.00 cm^{-1} which is the origin band of the transition of $1^2A_2 \rightarrow 1^2B_2$.

of electric discharge of *o*-xylene was also optimized to produce the least amount of CH radical which emits very strong fluorescence[20] in the visible region. The typical operating condition was 4-6 mA discharge current at the 1000 V dc potential. The distance of the anode electrode to the nozzle opening has been proven to be critical for the stability of the discharge over a long period. Thus, the stainless steel anode was firmly fixed into the center of the nozzle by means of the teflon holder. The backing pressure of the nozzle was measured to be about 2 atm. The pressure in the expansion chamber during operation was maintained to lower than 1.0 Torr using the mechanical vacuum pump. For increased collection of the fluorescence, a quartz lens ($f=5.0$ cm, $d=3.8$ cm) was placed inside the vacuum chamber. An area of the jet below the nozzle orifice of 2 mm in diameter 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. The interference signal was supplied to the computer for Fourier transform process. 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.[21] The high resolution spectrum shown in Figure 2 was obtained at the resolution of 0.05 cm^{-1} over 30 min.

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

Position[a]	Relative Intensity[b]	Spacing from the Origin[c]	Assignments
21824.67	2.95	479.67	$6a^0_1$
21535.81	0.72	190.81	$\alpha=-190.81$
21345.00	100.00	0	Origin band 0^0_0
21324.01	2.91	20.99	
21307.92	2.33	37.08	
21303.39	2.30	41.61	
21282.81	4.75	62.19	$\beta=62.19$
21262.99	1.76	82.01	
21242.56	3.11	102.44	$6a^1_1$
21153.52	1.43	191.48	$6a^2_2$
21046.58	3.00	298.42	$6b^0_1+6a^2_2$, $\delta=298.42$
21036.46	1.69	308.54	
20950.58	2.08	394.42	$16b^0_1$
20933.86	3.10	411.14	$16a^0_1$
20846.53	31.40	498.47	$6b^0_1$
20808.20	1.53	536.80	
20784.61	2.49	560.39	$16a^0_1+\gamma$, $\gamma=149.25$
20764.99	7.12	580.01	$6a^0_1$
20743.30	1.69	601.7	$16a^0_1$-α
20680.38	1.17	664.62	$6a^1_2$
20609.51	23.70	735.49	1^0_1
20547.32	2.74	797.68	$16b^0_2$, $16b^0_1+\delta$
20526.80	1.38	818.2	$16a^0_2$
20498.32	2.70	846.68	12^0_1
20467.23	1.76	877.77	
20435.23	1.67	909.77	
20397.98	1.41	947.02	
20380.54	1.98	964.46	$9b^0_1$-β, $16a^0_2+\gamma$
20360.11	1.93	984.89	5^0_1
20347.63	4.44	997.37	$6b^0_2$
20310.60	3.27	1034.4	$9b^0_1$
20294.66	2.80	1050.34	
20266.45	1.76	1078.55	
20214.93	1.80	1130.07	$9a^0_1$, $1^0_1+16b^0_1$
20198.84	2.43	1146.16	$6a^0_2$
20163.22	3.11	1181.78	15^0_1
20112.24	4.90	1232.76	$1^0_1+6b^0_1$, $16a^0_3$
20079.33	7.88	1265.67	$7a^0_1$
20055.11	1.51	1289.89	3^0_1, $6b^0_2+\delta$
20042.81	1.48	1302.19	
20029.43	1.43	1315.57	
20017.14	1.18	1327.86	14^0_1
19931.90	1.74	1413.10	
19882.54	3.52	1462.46	1^0_2 $(19a^0_1)$
19859.40	1.05	1485.60	$6b^0_3$
19848.64	1.11	1496.36	$19b^0_1$
19813.59	2.22	1531.41	$8b^0_1$
19773.16	2.88	1571.84	$8a^0_1$ $7a^0_1+y$, $y=306.17$
19729.15	0.83	1615.85	
19665.23	1.10	1679.77	12^0_2
19644.95	0.77	1700.05	$6a^0_3$
19614.96	0.84	1730.04	

Results and Discussion

Figure 1 shows the low resolution visible electronic emission spectrum of *o*-xylyl radical generated by an electric dc discharge of *o*-xylene. Of the spectral region scanned, most of the vibronic bands have been seen in the frequency region of 19,000-22,000 cm^{-1}. The width of the bands has been narrowed by rotationally cooling with a supersonic expansion. The rotational temperature of the radical is believed to be

19580.98	1.93	1764.02	$15^0_1+6a^0_1$
19556.12	0.75	1788.88	$6b^0_2+\delta$
19499.44	0.88	1845.56	$1^0_2+16b^0_1$
19383.91	0.68	1961.09	$1^0_2+6b^0_1$
19380.36	0.90	1964.64	5^0_2
19343.46	0.74	2001.54	$9b^0_2-\beta$
19274.58	0.63	2070.42	$9b^0_2$, $15^0_1+6a^0_1+y$

[a] In units of cm^{-1}. [b] Determined from the comparision with the origin band. [c] Measured in cm^{-1} from the origin of the 0-0 transition (21,345.00 cm^{-1}).

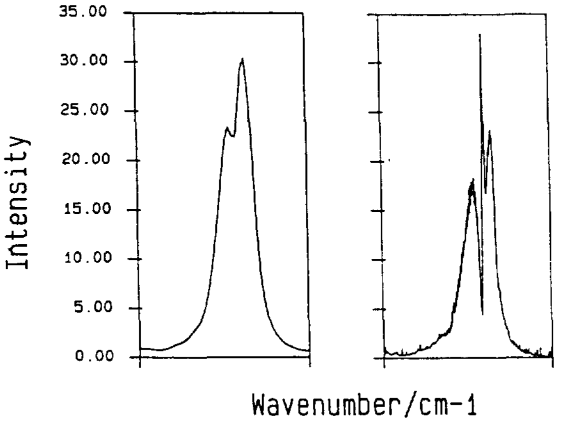

Figure 2. Comparison of the bandshape of the electronic origin band of the o-xylyl radical taken at low resolution (left side) with that at high resolution (right side). From this, it can be clearly seen that the peak at the high frequency side splits into 2 peaks with increasing resolution. The frequency range of the spectra is from 21,325 to 21,360 cm^{-1}.

about 50 K from the analysis of rotational contour of high resolution spectra of the benzyl radical obtained under a similar condition.[22] 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 $A^2\Delta\rightarrow X^2\Pi$ transition overlap with those of the o-xylyl radical.

The accurate frequencies of vibronic bands have been determined by measuring the frequency of the band origin which is supposed to lie in the minimum intensity point between two branches. The peak of maximum intensity is considered to arise from R subbranches of low K_a.

Table 1 lists the frequencies of the transitions observed, together with the relative intensities of the peaks measured in this work. The band with the highest intensive peak is located at 21345.00 cm^{-1}, which has been already assigned[14] as the electronic origin band of the 1^2A_2-1^2B_2 transition of the o-xylyl radical. The assignment of the vibronic bands observed has been carried out by means of not only the bandshape analysis but also the known vibrational frequencies obtained using a matrix isolation method.[12]

It should be understood that the shape of the contour is strongly dependent on the rotational constants, rotational temperature, and particularly the transition selection rules. For the case of benzyl radical, the vibronic bands are clearly

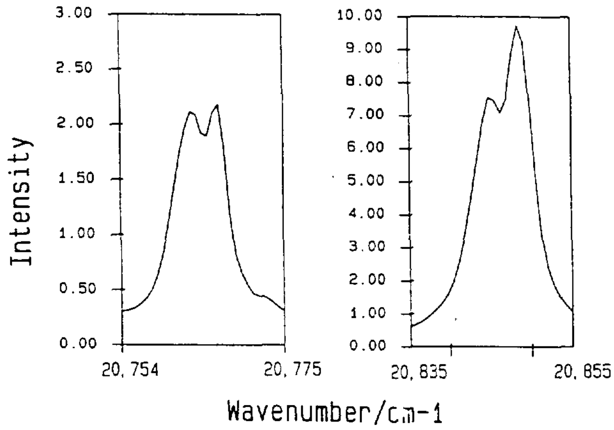

Figure 3. Observation of various kinds of the bandshapes for different normal modes of vibration which are coupled with the electronic transition moment of o-xylyl radical. The band on the left side is from $6a^0_1$, while that on the right side is from $6b^0_1$.

of type B or type A since the transition moment lying in the molecular plane is parallel to the b and the a inertial axes for the direction of the $^2A_2$-$^2B_2$ and $^2B_2$-$^2B_2$ electronic transitions, respectively.[3] And it has been observed[7] from the emission spectra of the benzyl radical that type A and type B bands split into 2 and 3 branches with increasing resolution, respectively.[3]

Cossart-Magos *et al.*[1] proved that the direction of the transition moment of the o-xylyl radical is oriented at +37° or −37° with respect to the b inertial axis upon the pure electronic excitation. Thus, all vibronic bands involving in-plane vibrations, as well as the electronic origin band will be presumed to have a hybrid character between type B and type A. It is therefore expected that the hybrid bands of o-xylyl resolve into 3 branches in the high resolution spectra. Figure 2 shows the bandshape of the o-xylyl radical, in which the band splits into 3 components at higher resolution, while it resolves into only 2 components at the low resolution which has been employed in this study. Moreover, it can be easily found that the peak on the higher frequency side splits further at the high resolution spectrum.

When the transition moment of the vibrational motion combines with that of the electronic transition, the direction of transition moment of o-xylyl may change its direction slightly. Hence, the rotational contours of vibronic bands are different in appearance for different normal modes of vibration. Figure 3 shows the typical appearance of the vibronic bands which is useful for identifying the vibrational modes qualitatively. The band $6a^0_1$ shows slightly different bandshape from the band $6b^0_1$. The band $6a^0_1$ exhibits a comparable intensity between both peaks, while the band $6b^0_1$ shows stronger intensity at the peak of higher frequency. The origin and 1^0_1 bands have a similar bandshape to the $6b^0_1$ band.

From the analysis of the peak frequencies and the bandshapes, it has been found that the frequencies of the $6b^0_1$ and $6a^0_1$ bands in the 1^2A_2-1^2B_2 electronic transition are located at 20,846.53 and 20,764.99 cm^{-1}, respectively. The hot vibronic band ($6a^1_0$) has been also identified at 21,824.67 cm^{-1}. Combination of the $6a^0_1$ with $6a^0_1$ gives an identification of the $6a^0_1$ band located at 21242.56 cm^{-1}. The assignments

Table 2. Vibrational Frequencies of *o*-Xylyl Radical in the Gas Phase[a]

Vibrational Mode	This Work	Previous Work[b]	*o*-Xylene[c]
1	735.49	737	735
2	–	3029	3018
3	1289.89		1290
4			702
5	984.89		986
6a	580.01	579	582
6b	498.47	500	506
7a	1265.67	1267	1223
7b			3345
8a	1571.84	1568	1583
8b	1531.41	1540	1609
9a	1130.07	1122	1155
9b	1034.4	1043	406
10a			325
10b			180
11			741
12	846.68	842	826
13			1185
14	1327.86		1323
15	1181.78	1184	255
16a	411.14	411	
16b	394.42		433
17a			862
17b			931
18a			1118
18b			1020
19a	1462.46	1462	1468
19b	1496.36		1494
20a			3064
20b			3018
6a[d]	479.67		

[a] In units of cm^{-1}. [b] Ref. (12). [c] Ref. (25). [d] Vibrational mode at the excited electronic state.

of the vibronic band observed in this work is also listed in Table 1. From these assignments, we have found several progressions and combinations of the normal modes of vibration. In this work, however, it is impossible to assign all of the bands observed since there are numerous ways of combinations.

With 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 *o*-xylyl radical in the gas phase. From the comparison of the vibrational frequencies, it has been clearly seen that most of the frequencies determined in this work are in good agreements with those obtained from the previous work of the matrix isolation method.

As for the benzene derivatives, it has been well-known that the isodynamic molecular approximation[23,24] is very useful for the estimation of the vibrational frequencies of the corresponding radicals. From the comparison of the vibrational frequencies of the *o*-xylyl radical with those[25] of the *o*-xylene in Table 2, we have concluded that the isodynamic molecular approximation can be applied to the vibration of the *o*-xylyl radical.

Summary

In the present work, rotationally cooled visible electronic emission spectra of the *o*-xylyl radical have been observed in a jet using an electric dc discharge of the parent compound *o*-xylene. Good assignments of the vibronic bands have been made on the basis of the bandshape, together with the data from the previous matrix isolation method. From the analysis of the spectra, the accurate frequencies of noraml modes of vibration of *o*-xylyl have been obtained in the ground and lowest excited electronic states.

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