The Near Ultraviolet Absorption Spectrum of *p*-Cresol Vapor

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Introduction

The near ultraviolet absorption by *p*-cresol in the vapor phase, extending in the spectral region between 2480 and 2950 A., and having the strongest band corresponding to the 0,0 vibrational transition at 2829 A., was studied by Purvis and McCleland,(1) and by Savard.(2) Savard's photograph of this absorption system is reproduced in Sponer and Teller's surveying article on "The Electronic Spectra of Polyatomic Molecules".(3) Robertson and his coworkers(4) utilized the spectra of *p*-, *o*-, and *m*-cresol vapors for their quantitative chemical analysis of synthetic cresol mixtures, and also reproduced their spectrograms in their paper.

As to the more modern interpretation of the origin of the *p*-cresol spectrum, Sponer,(5) and Cave and Thompson,(6) both on re-examining

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(1) J. Purvis and N. McCleland, *J. Chem. Soc.*, **103**, 1088 (1913).

(2) J. Savard, *Ann. de chim.*, **11**, 287 (1929); *Compt. rend.* **188**, 762 (1929).

(3) H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 75 (1941), on page 120.

(4) W. W. Robertson, N. Ginsburg, and F. A. Matsen, *Ind. Eng. Chem.*, **18**, 746 (1946).

(5) H. Sponer, *J. Chem. Phys.*, **10**, 672 (1942).

(6) W. T. Cave and H. W. Thompson, Farad. Soc. Discussions, 1950, p. 35.

Savard's published data, found out several conclusive features completely in line with results obtained recently for many of closely related molecules, *i. e.* mono- and di-substituted benzenes.

Savard's work, while appearing to contain the most reliable experimental informations on this spectrum so far published, gives us only three or four fundamental vibrational frequencies of the molecule, all of them belonging to the excited electronic state involved in the absorption transition. In order to complete the observational data for this band system, and also for the corresponding systems of *o*- and *m*-cresols appearing in the same wave-lengths region, at least to the extent achieved for their parent substance toluene,(7) we have photographed them anew, varying the concentration of the absorbing molecules in much wider range than by the previous workers. In this paper results of analysis for the *p*-cresol spectrum will be reported.

Experimental

For photographing the cresol vapor spectra a laboratory-built quartz spectrograph having a 120 cm. focus (for visible light) camera lens and a mean linear dispersion of 6 A. per mm. in this region was employed. The light source, absorption cell, and procedures of photography etc. are the same as described in our previous paper published in this journal on the near ultraviolet absorption spectra of acetophenone and other vapors.(8)

Commercial *p*-cresol sample supplied by Kanto-Kagaku Chemcals Mfg. Co. was used after several careful distillations in air. Unfortunately a very small trace of *o*-cresol could not be completely removed by such ordinary distillations, and a few of the strongest bands due to the latter isomer were recorded on some of our spectrograms. These could easily be identified and eliminated by comparing with our measurements of *o*-cresol bands, except perhaps in several cases where the close superposition might have affected the measured *p*-cresol wave-lengths slightly.

Exposures were made at the following temperatures of the liquid reservoir (Table 1), but the vapor filling the absorption cell (length 40 cm.) was always kept at a temperature 5 to 10 degrees higher than that of the liquid reservoir to prevent condensation on the windows and wall of the cell.

The finer details of the structure on the shorter wave-length side of the 0,0 band are best observed on exposures made at temperatures below 60°C. At higher temperatures the absorption in this region becomes so intense that a complete continuum results, and as we elevate the temperature and pressure, bands corresponding to excitations of higher frequency vibrations in the ground electronic state of the molecule gradually appear on the red end of the continuum. All bands of this system are degraded towards the longer wave-length side. Wave-lengths of band heads measured on different spectrograms are averaged and the correspondingv acuum wave-numbers are listed in Table 2. Head wave-lengths observed at very different vapor densities and temperatures may differ slightly from each other, depending mainly on different photographic densities, and, to some extent, on different developments of the rotational structure. But in the majority of cases they agree within 0.1 A. which is about the limit of accuracy of our measurements for sharp heads. A few bands, especially those "satellites" accompanying closely on the longer wave side of very strong bands, show no heads, and for them positions of maximum intensity are measured and given in Table 2 with the letter m affixed in the intensity column. In the notation adopted in the last column of the table, numbers standing on the left of the comma refer to excitations of ground state vibrations, and those on the right, to electronically excited state vibrations.

Interpretation of Spectrum and Discussion

The electronic transition responsible for this absorption system is an "allowed" one as in all substituted benzenes, and the 0,0 band must be the strongest, as the one at 35338 cm.$^{-1}$ actually is. Fundamental vibrational frequencies of the molecule participating in this transition are listed in Table 3 against the published Raman and infrared data observed in the liquid

The difference frequency -23 cm.$^{-1}$ used in the above analysis occurs always with satellite bands mentioned in the preceding section, for which heads could not be measured. If examined under much higher resolution, these bands would be more satisfactorily explained as arising from the 1-1 transition of a certain low frequency fundamental, or superposition of 1-1 transitions of several different fundamentals, accompanying each strong main transition.

The *p*-cresol molecule has, strictly speaking, no

Table 1

Temperature of liquid (°C.)	20	30	40	50	60	70	80	90	100	110	120	130	140
Saturated Vapor pressure (mm.Hg)	.08	.18	.40	.83	1.7	3.3	6.1	11	18	30	47	71	108

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(7) N. Ginsburg and W. W. Robertson, *J. Chem. Phys.*, **14**, 511 (1946).

(8) S. Imanishi, K. Semba, M. Ito and T. Anno, *This Bulletin*, **25**, 150 (1952).

Table 2

Near Ultraviolet Absorption Bands of *p*-Cresol Vapor.

m: Intensity-maxima data.

*: Measurement probably affected by superposition of a strong *o*-cresol band.

Wave-Number (cm.$^{-1}$)	Intensity, °C												Interpretation
	140	130	120	110	100	90	80	70	60	50	40	30	
(33964)	00	00											1374, 0; 3×458, 0
34004	00	00											839+499, 0
042	0	0											1296, 0; 2×648, 0
079	0	0	00										1259, 0
107	00	00											1231, 0
147	0	0											458+734, 0
186	3	2	00	00									1152, 0
226	5	4	0	00									2×230+648, 0; 648+458, 0
264	8	8	1	0	00								230+839, 0
339			8	0	00								2×499, 0
385				3	0								458+499, 0
423				10	3								2×458, 0
460				10	4								230+648, 0; 734+839.694
499				10	7	0	00	00					839, 0
562				10	2								2×734, 694
604					5								734, 0
654					10	00							230+458, 0
690						00							648, 0
718						00	00						2×310, 0; 839, 217
764						0							230+310+458, 422
804						4	0	00					310+648, 422
839						8	2	1					499, 0
880						10	5	2	0				458, 0; 1152, 694; 2×230, 0
940							0	00					2×230, 217
993							1	0					1152, 808
35028							5	4	00				734, 422, ; 310, 0
069								3	0				230+734, 694
108							10	7	3	1	00		230, 0; 648, 422
179									2	0	00		159, 0: 230+734, 808
229									4	2	00		1259, 1153
261								10	10	7	3	1	499, 422
283												3	230+734, 217+694
298										10	7	5	734, 694
308										7m	4m	5m	839, 808
317											5m	4m	0, −23
338									10	10	10	8	0, 0
397							10	7	2	1	0	00	159, 217
469							5	3	00				458, 585
515								4	0				734, 217+694
536								3	0				499, 694
555							8	5	2	0	00		0, 217
650									2	00	00		839, 1153; 499, 808
686									3	0	00		458, 808
719									3	1	0		734, 422+694
725									1m	00m			839, 1226; 1152, 1536; 310, 694; 1231, 2×808
738									2m	0m			0, 422-23
760								10	5	2	1	1	0, 422; 734, 1153
(807)								3	0				1152, 2×808
879									0				
901									0	00			

Wave-Number (cm⁻¹)	Intensity, °C 140	130	120	110	100	90	80	70	60	50	40	30	Interpretation
35923									2	0	00		0, 585
981									1	0	00		0, 217+422
36032										2	0	00	0, 694; 458, 1153
068									10	8	3	2	499, 422+808
103											8	2	734, 694+808; 458, 1226
109											3m	2m	458, 422+808
120											3m	2m	0, 808-23; 839, 2×808
146									10	10	10	8	0, 808
205*									4	3	1	0	159, 217+808
294									2	2	1	0	458, 217+1196
354*										7*	5*	4*	0, 217+808
454									4	1	0		499, 2×808
491									5	3	2		0, 1153; 458, 2×808
534									8	6	4	3	0, 1196; 839, 808+1226; 1231, 3×808
564									6	4	2	1	0, 1226; 310, 1536; 0, 422+808
610									5	4	2	2	0, 1272; 1152, 3×808
730									0	00	00		0, 585+808; 0, 2×694; 230, 2×808
830*									4	3	2	0	0, 217+1272
874									5	3	1	00	0, 1536; 499, 1226+808
918									7	5	3		458, 422+2×808; 734, 694 +2×208; 839, 3×808
955*									8	7	5	3	0, 2×808
37011*									1	0	0		159, 217+2×808
176*									0	00	00		0, 217+2×808
258*									0	00	00		499, 3×808;
305*									1	0			458, 3×808; 0, 1153+808; 0, 694+1272
318									3	1			0, 1196+808-23
341											1		0, 1196+808; 839, 1126 +2×808; 1231, 4×808
375									2	1			0, 422+2×808; 0, 1226+808
420								10	3	2	2	0	0, 3×694; 0, 1272+808; 1152, 4×808
476								3	1	00	00		499, 217+3×808
629								5	3	2	1	0	0, 217+1272+808
679*									2	0			0, 1536+808
723									2	1			734, 694+3×808; 839, 4×808
763								10	3	3	1	0	0, 3×808; 0, 1153+1272
807									4	2	0	00	0, 1196+1272
921*								3	1	0	00	00	648, 4×808
975								0	00	00			0, 217+3×808
38072*								8	3	1	1	0	499, 4×808; 0, 1196+1536
111								4	2	0	00		458, 4×808; 0, 4×694
148								5	2	0	00		0, 1196+2×808
197								2m	0m				1152+839, 6×808
227							5	5	2	0	0	00	0, 1272+2×808; 1152, 5×808
272							6	4	0				648, 1153+3×808
350							4	0					230, 4×808
410*							6	4	00				0, 2×1536
450							3	00					
469							3						
527							5	2	00				734, 694+4×808
567							6	5	1				0, 4×808
610							3	2	00				734+458, 422+5×808
(645)								0					734, 5×808

Wave-Number (cm^{-1})	Intensity, °C												Interpretation
	140	130	120	110	100	90	80	70	60	50	40	30	
38702							2	1					159+734, 217+5×808
786							1	00					0, 217+4×808
857							3	2					458+1296, 422+6×808
891							1	1					1296, 6×808
952							2	1					1231, 6×808; 0, 1196+3×808
39004							2	1					0, 2×1196+1272
042							00	00					0, 1272+3×808; 1152, 6×808
284							00	00					
346						7	1	1					839, 6×808
380						2	0	00					0, 5×808
362						3	0	0					458+734, 422+6×808
447						1	00	00					734, 6×808
494						2	00	00					
545						1							
(583)						1							(0, 217+5×808)
(647)						1							
(699)						1							(499, 6×808)
(795)							0						(0, 422+5×808)
(829)						0							(0, 1272+4×808; 1152, 7×808)
(887)						0							(310, 6×808)
(982)						00							(230, 6×808)
(40233)						00							(0, 6×808)

Table 3

Fundamental Vibrational Frequencies of *p*-Cresol Molecule.

Raman Effect (Liquid)					Ultraviolet Absorption (Vapor)				Infra-Red Abs. (Liquid)$^{(11)}$
$\Delta\nu$ (Intensity)$^{(9)}$		Depolarization Factor$^{(9)}$, ρ	Assignment$^{(10)}$ (C_{2v})		Ground State Present Work		Excited State Present Work	ref. 5,6	Ground State
					159				
					230	β_1 or α_2	217		
338	(4)	1.00	ω_{10},	β_I	310	β_1			
465	(5)	0.52	ω_{11},	α_1	458	α_1	422	419	
507	(0)				499				
649	(5)	0.92	ω_2,	β_1	648	β_1	585		
703	(0)	0.87							680～690 (w)
736	(1)				734	α_1	694		720～730 (w)
822	(3)	0.15							818 (st)
842	(10)	0.07	ω_1,	α_1	839	α_1	808	808	860～870 (w)
1016	(00)								910～920 (m) 1000～1010 (w) 1080 (m)
1171	(2)	0.34	δ_3,	α_1	1152				1170～1180 (st)
1214	(5)	0.09	ω_4,	α_1	1231		1153		
1256	(3)	0.07	ω_3,	α_1	1259		1196	1187	
1297	(0)	0.55			1296		1226		
1381	(3)	0.49			1374		1272	1268	
1450	(00)	0.92							
1615	(4)	0.74					1536		
2864	(1/2)	p							
2922	(2)	p							
3015	(1/2)	p							
3046	(3)	0.47							

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(9) K. W. F. Kohlrausch u. A. Pongraz, *Monatsh. f. Chem.*, **63**, 427 (1933).

(10) O. Paulsen, *Monatsh. f. Chem.*, **72**, 244 (1939).

(11) J. Lecomte, *J. Phys. radium*, **9**, 13 (1938).

symmetry element, but as far as the ultraviolet absorption is concerned, skeleton vibrations involving only heavy-atom-containing bonds chiefly come into question. In this sense the molecule has approximately the C_s or even C_{2v} symmetry if we take the oxygen atom of the OH group as lying in the ring plane. Then its mass distribution is nearly the same as in the p-fluorotoluene molecule, the ultraviolet absorption of which was investigated by Cave and Thompson in the vapor phase.(6) They found the following fundamental frequencies in this molecule.

p-Fluorotoluene. 0,0 band at 36876 cm.$^{-1}$

Excited State	185,	—,	—,	398,	584,	794,
Ground State	217,	311,	377,	453,	641,	825,

Excited State	843,	1014,	1194,	1229 cm^{-1}.
Ground State	844,	1156,		cm^{-1}.

From the close parallelism between these and the p-cresol fundamentals given in Table 3, we may identify 230 (217) cm.$^{-1}$ in p-cresol wlth 217 (185) cm.$^{-1}$ in p-fluorotoluene in mode of vibration, even though no corresponding Raman shifts are reported. At the same time we notice the characteristic structure-sensitiveness of this low-frequency fundamental in that its values are approximately in the inverse ratio of the masses of the OH group and the F atom in both the electronic states. There is another set of frequencies 734 (694) cm.$^{-1}$ in p-cresol and 825 (794) cm.$^{-1}$ in p-fluorotoluene, which, apparently, is also structure-sensitive, but in comparing the respective Raman values the physical correspondence of these fundamentals in the two molecules seems doubtful. Now the structure-sensitive 230(217)cm.$^{-1}$ frequency of p-cresol must be of the mode in which the C–OH bond chiefly changes, and we suggest that it is the bending of this bond in the ring plane (β_1 type) or perpendicular to it (α_2 type), the single quantum excitation of either of which can produce a transition moment with the elec tronic transition under consideration (A_1–B_1). This is supported by the fact that the manner in which the 217 cm.$^{-1}$ excited state frequency combines with other α_1 type fundamentals clearly indicates its non-totally symmetric nature (see Table 2).

In mono-substituted benzenes we find the analogous behavior of a low frequency fundamental around 200 cm.$^{-1}$, so far judged from vapor ultraviolet absorption data. Thus in phenol,(12) monofluorobenzene,(13) aniline,(14) benzaldehyde,(15) benzonitrile,(16) and benzotrifluoride(17) fundamental frequencies 245, 240 (assigned to α_2), 231, 223 (α_2 or β_1), 170 and 141 (assigned to β_1) cm.$^{-1}$, respectively, are reported. These are again in the inverse order of the masses of theOH, F, NH_2, CHO, CN and CF_3 groups or atom, and their corresponding Raman lines are all depolarized, suggesting their belonging to the similar bendings of the substitution bonds in these mono-substituted benzene molecules.

Returning to p-cresol, we have taken another low frequency fundamental 159 cm.$^{-1}$ in the ground state from the appearance and intensity of the 35179 cm.$^{-1}$ band on the longer wave-length side of the 0,0 band, although an alternative interpretation can be given to this band as shown in Table 2. The weakly excited β_1 type 310 cm.$^{-1}$ ground state frequency has its analogue 311 cm.$^{-1}$ in p-fluorotoluene, while their closely coinciding Raman counterparts are not found. Another β_1 type frequency 648 (585) cm.$^{-1}$, which originated from the e_g^+ type 606 cm.$^{-1}$ degenerated vibration in benzene is also weakly excited in both states. Correspondence between other structure-insensitive fundamentals and the Raman values is generally good as we see in Table 3.

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(12) F. A. Matsen, N. Ginsburg, and W. W. Robertson, *J. Chem. Phys.*, **13**, 309 (1945).

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(15) S. Imanishi, *J. Chem. Phys.*, **19**, 389, (1951)

(16) H. C Hirt and J. P. Howe, *J. Chem. Phys.*, **16**, 480 (1948).

(17) H. Sponer, *J. Opt. Soc. Am.*, **39**, 840 (1949); also reference (6).