

Vibrational and electronic absorption spectra of 4-chloro 2-methyl, 4-chloro 3-methyl and 6-chloro 3-methyl phenols

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Abstract. The infrared spectra of 4-Cl 2-Me, 4-Cl 3-Me and 6-Cl 3-Me phenols have been recorded. The vibrational spectrum has been analysed assuming that the molecules belong to C_s point group and a tentative assignment of the observed frequencies to various modes of vibration has been proposed. The near ultraviolet absorption spectrum of these compounds has also been recorded. Assuming the transition to be electronically allowed the strongest band on the longer wavelength side has been assigned as the (0, 0) band in each case. The spectrum has been analysed in terms of several excited state frequencies which have been correlated with the ground state frequencies observed in the infrared spectrum.

Keywords. Infrared ; ultraviolet absorption ; electronic absorption ; vibrational analysis.

1. Introduction

Spectroscopic studies of chloro and methyl phenols have been reported in the literature (Green and Harrison 1971 ; Rao 1962 ; Cave and Thompson 1950 ; Green 1962). However no study of the spectroscopic properties of di-substituted phenol containing both chlorine and methyl substituents has been reported so far. This prompted us to undertake the spectroscopic study of several chloro-methyl phenols. The results of our study of the infrared and the near ultraviolet absorption spectra of 4-Cl 2-Me, 4-Cl 3-Me and 6-Cl 3-Me phenols are presented here.

2. Experimental

Pure samples of the compounds under investigation were obtained from Dr. Theodor Schuchardt, Munchen. All the three compounds are solid at room temperature (30-40° C).

The infrared spectra were recorded on Perkin-Elmer infrared spectrophotometer (Model 621) in the range (200-4000 cm^{-1}) using Nujol Mull solution.

The ultraviolet absorption spectra were recorded on Hilger medium quartz spectrograph. The compounds were kept in an absorption cell of length 125 cm and diameter 2.5 cm. The temperature of the cell could be varied and it was found that the absorption spectra were best developed when the temperature was 40° C. A 150 W Beckman hydrogen lamp was used as a source of continuum and exposure time of 40 min was found sufficient to record the spectra on Ilford special rapid plates with sufficient intensity. The spectra were measured from positive prints using a comparator with a least count of 10⁻⁴ mm. The infrared absorption spectra of 4-Cl 2-Me, 4-Cl 3-Me and 6-Cl 3-Me phenols are shown in figures 1a, 1b and 1c.

3. Results and discussion

3.1. Infrared spectrum

It is customary to treat each multiatomic substituent, e.g., CH₃ or OH as a point mass so that all substituted benzenes have only 30 normal modes of vibration. Since the molecules under consideration are assumed to belong to C_s point group, 21 of these vibrations would be (a') planar and 9 (a'') non-planar. In addition to these 30 vibrations there would be 12 additional vibrations due to the internal

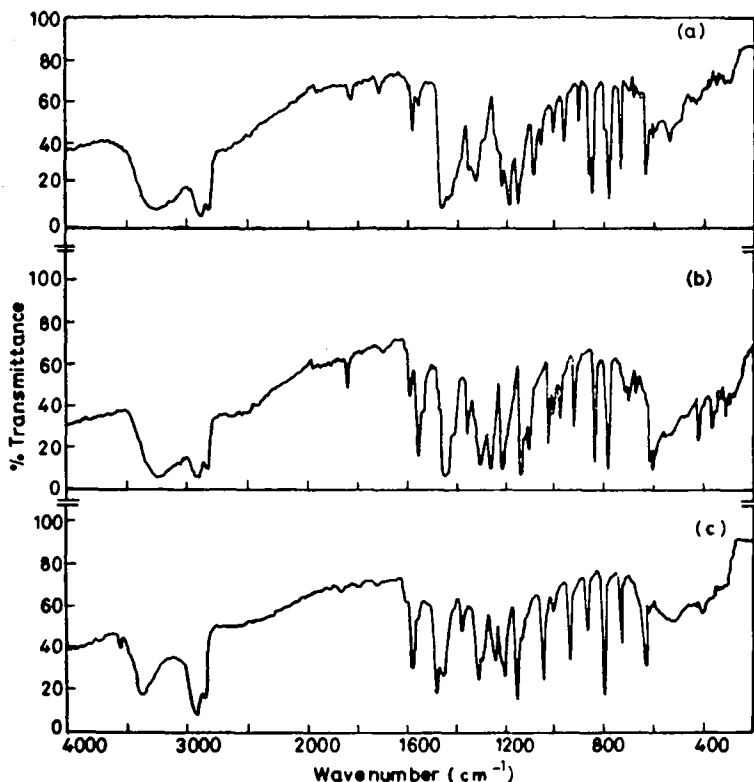


Figure 1. Infrared absorption spectrum, a. 4-chloro 2-methyl phenol; b. 4-chloro 3-methyl phenol; c. 6-chloro 3-methyl phenol.

motion in the substituents. For C_6 point group all the vibrations, i.e., whether they are of type a' or a'' are both infrared and Raman active.

Varsanyi (1969) developed a system of classifying a substituent as either "light" or "heavy" to systematise the assignments of observed frequencies in substituted benzenes to the various benzene modes. On the basis of this classification he suggested suitable ranges of frequencies to which the various benzene type modes should be assigned in the spectrum of substituted benzene. In making the assignments in the present work we have kept in mind these suggestions of Varsanyi (1969) and have also considered the assignments suggested by earlier workers in ortho and meta cresols (Rao 1962), para-chloro phenol (Green and Harrison 1971), 2,3-dichlorophenol (Sanyal and Pandey 1973) and chloro-methyl aniline (Sharma and Dwivedi 1976). The proposed assignments are given in table 1.

3.1a. *Stretching vibrations $\nu(C-H)$ and $\nu(C-X)$.* Out of six C-H stretching modes appearing in benzene three are transformed into three C-X stretching modes. In the present set of molecules these involve C-OH, C-CH₃ and C-Cl stretching modes.

Bellamy (1964) and Rao (1963) have suggested that C-Cl stretching vibration in substituted benzene appears in the frequency range 600-800 cm⁻¹. It is also expected to appear very prominently in the infrared spectrum. In the present investigation one infrared band has been observed in the above frequency range with large intensity in all the three compounds and has been explained as being due to C-Cl stretching mode.

C-CH₃ stretching vibration causes strong absorption in the range 1150-1200 cm⁻¹ (Sharma and Dwivedi 1976). This stretching frequency has been assigned at 1195 cm⁻¹ for 4-Cl 2-Me and at 1190 cm⁻¹ for 6-Cl 3-Me phenol.

Numerous investigators (Sanyal and Pandey 1973; Mecke and Rassmy 1955; Bellamy and Davis 1948) assigned a band near 1250 cm⁻¹ as due to C-OH stretching vibration in substituted benzenes containing OH group. We have assigned the bands at 1250, 1235 and 1250 cm⁻¹ to this mode in 4-Cl 2-Me, 4-Cl 3-Me and 6-Cl 3-Me phenols respectively.

Three $\nu(C-H)$ stretching vibrations are also expected in addition to three $\nu(C-X)$ stretching vibrations already discussed above. These vibrations usually appear in the region 3000-3100 cm⁻¹ and are easily assigned as shown in table 1.

3.1b. *Stretching vibrations $\nu(C-C)$:* Except for the totally symmetric ring breathing (mode 1) vibration all the remaining five C-C stretching vibrations in benzene appear in the frequency range 1300-1600 cm⁻¹ (Varsanyi 1969). Some of these vibrations are significantly affected in magnitude on substitution, while the others remain almost unchanged. The assignments of these modes to the various observed frequencies on the basis of similar assignments by other workers (Sanyal and Pandey 1973; Sharma and Dwivedi 1976) are as shown in table 1. The ring breathing vibration is also greatly affected. We have chosen the frequencies 1035 cm⁻¹, 1045 cm⁻¹ and 1040 cm⁻¹ involved in bands which appear with large intensity as the ring breathing frequency of 4-Cl 2-Me, 4-Cl 3-Me and 6-Cl 3-Me phenol respectively.

3.1c. *Ring in-plane bending $\phi(C-C-C)$ vibrations.* There are three (C-C-C) in-plane bending vibrations in substituted benzenes. The assignments of these

Table 1. Infrared absorption of 4-Cl 2-Me, 4-Cl 3-Me and 6-Cl 3-Me phenols

Mode (Wilson's)	4-Cl 2-Me Phenol		4-Cl 3-Me phenol		6-Cl 3-Me phenol		Assignments
	frequency in cm ⁻¹	Int.	frequency in cm ⁻¹	Int.	frequency in cm ⁻¹	Int.	
20a	3610	s	3610	s	3560	vs	$\nu(\text{O-H})$ stretching
2	3100	vw	3090	vw	3080	vw	$\nu(\text{C-H})$ stretching
20b	3060	vw	3060	vw	$\nu(\text{C-H})$ stretching
	3030	vw	3030	vw	3040	vw	$\nu(\text{C-H})$ stretching
	2960	vw	2960	vw	2960	w	ν_{as} in CH ₃ group
	2860	w	2850	vw	2850	vw	ν_s in CH ₃ group
8b	1610	s	1605	w	1605	w	$\nu(\text{C-C})$ stretching
8a	1580	w	1575	vs	1585	vs	$\nu(\text{C-C})$ stretching
19a	1485	vs	1472	w	1480	s	$\nu(\text{C-C})$ stretching
	1440	vs	1445	vw	1440	s	δ_{as} in CH ₃ group
19b	1400	vs	1410	s	1410	w	$\nu(\text{C-C})$ stretching
	1375	s	1370	s	1370	s	δ^+ in CH ₃ group
	1345	w	1340	w	1340	w	δ_{as}^- in CH ₃ group
14	1310	s	1305	vs	$\nu(\text{C-C})$ stretching
3	1270	sh	1275	vvs	1285	s	$\beta(\text{C-H})$ i.P. bending
7a	1250	vs	1235	vs	1250	vs	$\nu(\text{C-OH})$ stretching
13	1195	vvs	1190	vvs	$\nu(\text{C-CH}_3)$ stretching
	1150	vvs	1150	vvs	1150	vvs	$\beta(\text{OH})$ i.P. bending
15	1100	vvs	1120	s	1125	s	$\beta(\text{C-H})$ i.P. bending
18b	1080	sh	1075	w	1085	vw	$\beta(\text{C-H})$ i.P. bending
1	1035	s	1045	vs	1040	s	Ring breathing
	1025	s	1025	s	Rocking in CH ₃
	985	s	995	s	995	s	δ_{as}^- in CH ₃
17b	935	vw	935	s	935	s	$\gamma(\text{C-H})$ O.P. bending
5	865	vs	855	s	855	s	$\gamma(\text{C-H})$ O.P. bending
11	800	s	805	s	795	vvs	$\gamma(\text{C-H})$ O.P. bending
12	755	vs	765	w	750	s	$\phi(\text{C-C-C})$ i.P. bending
4	715	vw	720	s	720	sh	$\delta(\text{C-C-C})$ O.P. bending
6b	700	w	690	s	695	vw	$\phi(\text{C-C-C})$ i.P. bending
7b	650	vs	630	vs	630	vs	$\nu(\text{C-Cl})$ stretching
	610	w	610	w	610	vw	$\gamma(\text{OH})$ O.P. bending
16a	580	w	570	w	580	w	$\delta(\text{C-C-C})$ O.P. bending
6a	550	s	550	w	545	w	$\phi(\text{C-C-C})$ i.P. bending
16b	440	w	440	vw	445	vw	$\delta(\text{C-C-C})$ O.P. bending
9b	385	w	385	s	390	vw	$\beta(\text{C-CH}_3)$ i.P. bending
10a	355	w	355	w	350	vw	$\gamma(\text{C-OH})$ O.P. bending
9a	310	w	310	w	305	vw	$\beta(\text{C-Cl})$ i.P. bending
10b	260	w	260	w	265	w	$\gamma(\text{C-CH}_3)$ O.P. bending
15	250	w	250	w	$\gamma(\text{C-OH})$ O.P. bending
17a	230	w	$\gamma(\text{C-Cl})$ O.P. bending

frequencies as given in table 1 are based on the assignments made by earlier workers and the frequency ranges suggested by Varsanyi (1969).

3.1d. *In-plane bending $\beta(C-H)$ and $\beta(C-X)$ vibrations.* In general for trisubstitution C-H in-plane bending vibrations appear in the frequency range 1070-1300 cm^{-1} (Varsanyi 1969). Earlier work on chlorinated methyl anilines has ascribed, C-Cl in-plane bending mode to a frequency observed at 300 cm^{-1} while C-CH₃ in-plane bending has been assigned at 380 cm^{-1} . The C-OH in-plane bending vibration has been assigned at 245 cm^{-1} in phenol. Our assignments given in table 1 are in general agreement with the above.

3.1e. *Out-of-plane bending $\delta(C-C-C)$ vibrations.* There are three (C-C-C) out-of-plane bending vibrations in substituted benzenes. In general for trisubstitution these vibrations appear in the frequency range 420-700 cm^{-1} (Varsanyi 1969). We have also observed these frequencies in the suggested range.

3.1f. *Out-of-plane bending $\gamma(C-H)$ and $\gamma(C-X)$ vibrations.* According to Randle and Whiffen (1955) the C-H out-of-plane deformations generally appear in the range 750-1000 cm^{-1} in the infrared spectra of substituted benzenes. C-X out-of-plane bending vibrations are generally observed at very low frequencies. Their assignments are also included in table 1.

The internal vibrations of CH₃ and OH groups have also been assigned in analogy with earlier assignments.

3.2. Ultraviolet absorption spectrum

The electronic absorption bands of 4-Cl 2-Me, 4-Cl 3-Me and 6-Cl 3-Me phenol lie in the region 290-260 nm. The transition is the analog of 260 nm transition in benzene, but it is expected to show the features of an allowed transition because of the reduced symmetry of the present compounds. These features include a strong (0,0) band on the longer wavelength side of the electronic transition, and appearance of prominent bands involving totally symmetric vibrations. The ultraviolet absorption spectrum of 4-Cl 2-Me, 4-Cl 3-Me and 6-Cl 3-Me phenols is shown in figures 2a, 2b and 2c.

On the longer wavelength side of the absorption spectrum, a very strong band has been observed at 34890, 34934 and 35595 cm^{-1} for 4-Cl 2-Me, 4-Cl 3-Me and 6-Cl 3-Me phenols respectively. These are the strongest bands of the respective absorption spectrum and appear with very good intensity even at the lowest pressure of the absorbing vapour. They have been taken as the (0,0) bands for the three different compounds.

Three hot bands involving three low lying ground state vibrations have been observed in the spectrum of 4-Cl 2-Me and 6-Cl 3-Me phenol. These vibrations have the magnitudes 150, 315 and 441 cm^{-1} and 139, 232 and 305 cm^{-1} respectively in the two compounds. Four hot bands have been observed in the spectrum of 4-Cl 3-Me phenol involving ground state vibrations of magnitude 181, 273, 350 and 436 cm^{-1} . In addition to these ground state vibrations several excited state

fundamental frequencies have been observed with magnitude 254, 399, 463, 590, 634, 741, 979, 1080, 1135, 1222 and 1351 cm^{-1} in 4-Cl 2-Me phenol, 263, 336, 420, 621, 712, 929, 1130, 1235 and 1367 cm^{-1} in 4-Cl 3-Me phenol and 466, 552, 626, 696, 973, 1052, 1189, 1234 and 1382 cm^{-1} in 6-Cl 3-Me phenol. The ultraviolet bands and their assignment in terms of the above frequencies are given in table 2.

The excited state fundamentals have been tentatively correlated with the ground state frequencies as shown in table 3.

Table 2. Ultraviolet absorption of 4-Cl 2-Me phenol.

Position of bands (cm^{-1})	Rel. Int.	Separation from (0, 0) band	Assignments
34449	vw	0- 441	0- 441
34575	vw	0- 315	0- 315
34740	w	0- 150	0- 150
34821	ms	0- 69	0- 69
34890	vs	(0, 0)	(0, 0)
34965	ms	0+ 75	0+ 75
34995	ms	0+ 105	0+ 105
35144	w	0+ 254	0+ 254
35289	ms	0+ 399	0+ 399
35353	w	0+ 463	0+ 463
35480	ms	0+ 590	0+ 590
35524	ms	0+ 634	0+ 634
35631	s	0+ 741	0+ 741
35685	w	0+ 795	0+ 2 \times 399
35760	w	0+ 870	0+ 2 \times 399 + 75
35869	s	0+ 979	0+ 979
35968	ms	0+ 1080	0+ 1080
36025	w	0+ 1135	0+ 1135 or 741 + 399
36112	w	0+ 1222	0+ 1222
36241	s	0+ 1351	0+ 1351
36308	ms	0+ 1418	0+ 1351 + 75
36409	w	0+ 1519	0+ 1351 + 75 + 105
36545	w	0+ 1655	0+ 1080 + 590
36669	w	0+ 1777	0+ 1135 + 634
36803	vw	0+ 1913	0+ 1351 + 634 - 69
36853	vw	0+ 1963	0+ 2 \times 979
36974	vw	0+ 2084	0+ 1351 + 741
37233	vw	0+ 2343	0+ 1351 + 979
37333	vw	0+ 2443	0+ 1351 + 1080

Table 2. (Contd.)

Position of bands cm^{-1}	Rel. Int.	Separation from (0, 0) band	Assignments
UV absorption of 4-Cl 3-Me phenol			
34498	vw	0- 436	0- 436
34584	w	0- 350	0- 350
34661	w	0- 273	0- 273 or 0- 181-94
34753	s	0- 181	0- 181
34840	s	0- 94	0- 94
34934	vs	(0, 0)	(0, 0)
35022	s	0+ 88	0+ 88
35109	w	0+ 175	0+ 2×88
35197	w	0+ 263	0+ 263
35270	ms	0+ 336	0+ 336
35354	s	0+ 420	0+ 420
35555	s	0+ 621	0+ 621
35646	s	0+ 712	0+ 712
35863	ms	0+ 929	0+ 929
36064	s	0+ 1130	0+ 1130
36169	s	0+ 1235	0+ 1235, or 0+ 2×621
36301	s	0+ 1367	0+ 1367
36483	w	0+ 1549	0+ 929+621
36588	w	0+ 1654	0+ 929+712
36685	w	0+ 1751	0+ 712+621+420
36798	w	0+ 1864	0+ 2×929
36898	ms	0+ 1964	0+ 299+621+470
36996	ms	0+ 2062	0+ 1367+712
37226	ms	0+ 2292	0+ 1367+929
37343	ms	0+ 2409	0+ 1367+1130-94 or 1367+ 621+420
37583	w	0+ 2649	2+ 1367-94
37659	w	0+ 2725	0+ 2×1367
37951	w	0+ 3017	0+ 1367+929+712
38148	w	0+ 3211	0+ 1367+2×929
38362	vw	0+ 3433	0+ 2+1367+712
UV absorption of 6-Cl 3-Me phenol			
35289	vw	0- 305	0- 305
36363	w	0- 232	0- 232
35456	s	0- 139	0- 139
35517	vs	0- 77	0- 77
35594	vvs	(0, 0)	(0, 0)
35677	w	0+ 82	0+ 82
36062	vw	0+ 466	0+ 466
36147	s	0+ 552	0+ 552
36221	vs	0+ 626	0+ 626
36291	vs	0+ 696	0+ 696
36369	vvw	0+ 774	0+ 696+82
36462	vvw	0+ 867	0+ 696+2×82
36568	s	0+ 973	0+ 973

Table 2. (Contd.)

Position of bands cm^{-1}	Rel. Int.	Separation from (0, 0) band	Assignments
36646	s	0+ 1052	0+ 1052
36784	w	0+ 1189	0+ 1189
36828	ms	0+ 1234	0+ 1234
36919	ms	0+ 1325	0+ 699+626
36977	ms	0+ 1382	0+ 1382 or 2×696
37029	w	0+ 1435	0+ 973+466
37244	w	0+ 1650	0+ 1189+466
37302	w	0+ 1708	0+ 1234+466
37339	w	0+ 1744	0+ 1052+696
37463	vw	0+ 1868	0+ $2 \times 973 - 77$
37553	vw	0+ 1959	0+ 2×973
37655	vw	0+ 2060	
37918	vvw	0+ 2323	0+ $2 \times 973 + 466 - 77$ or 1382+973
38000	vvw	0+ 2406	0+ $2 \times 973 + 466$
38317	vvw	0+ 2722	0+ $2 \times 1052 + 626$

s = strong, vs = very strong, vvs = very very strong, ms = medium strong, w = weak, vw = very weak, vvw = very very weak.

Table 3. Correlation of frequencies in infrared and ultraviolet spectra.

4-Cl 2-Me phenol Electronic UV			4-Cl 3-Me phenol Electronic UV			6-Cl 3-Me phenol Electronic UV			Assignments
IR	GS	ES	IR	GS	ES	IR	GS	ES	
..	260w	273w	..	230w	139s
							232w		
310w	315vw	254w	305vw	305w	..	$\beta(\text{C}-\text{Cl})$
..	355s	350w	263w	$\gamma(\text{C}-\text{OH})$
440w	441vw	..	440w	436vw	336ms	$\delta(\text{C}-\text{C}-\text{C})$
..	545w	..	466vw	$\phi(\text{C}-\text{C}-\text{C})$
650vs	..	590ms	630vs	..	552s	$\nu(\text{C}-\text{Cl})$
700w	..	634ms	690s	..	621s	695vs	..	626vw	$\phi(\text{C}-\text{C}-\text{C})$
800s	..	741s	805s	..	712s	855s	..	696vs	$\gamma(\text{C}-\text{H})$
1035s	..	979s	1045s	..	929ms	1040s	..	973s	Ring breathing
..	1125s	..	1052s	$\beta(\text{C}-\text{H})$
1150vs	..	1080ms
			1235vs	..	1130s	1250vs	..	1189w	$\nu(\text{C}-\text{OH})$
1195s	..	1135w	$\nu(\text{C}-\text{CH}_3)$
..	1340w	..	1235s	1340w	..	1234ms	δ_{as} in CH_3
1485vs	..	1351s	1472w	..	1367w	1480s	..	1382ms	$\nu(\text{C}-\text{C})$

GS, ground state; ES, excited state.

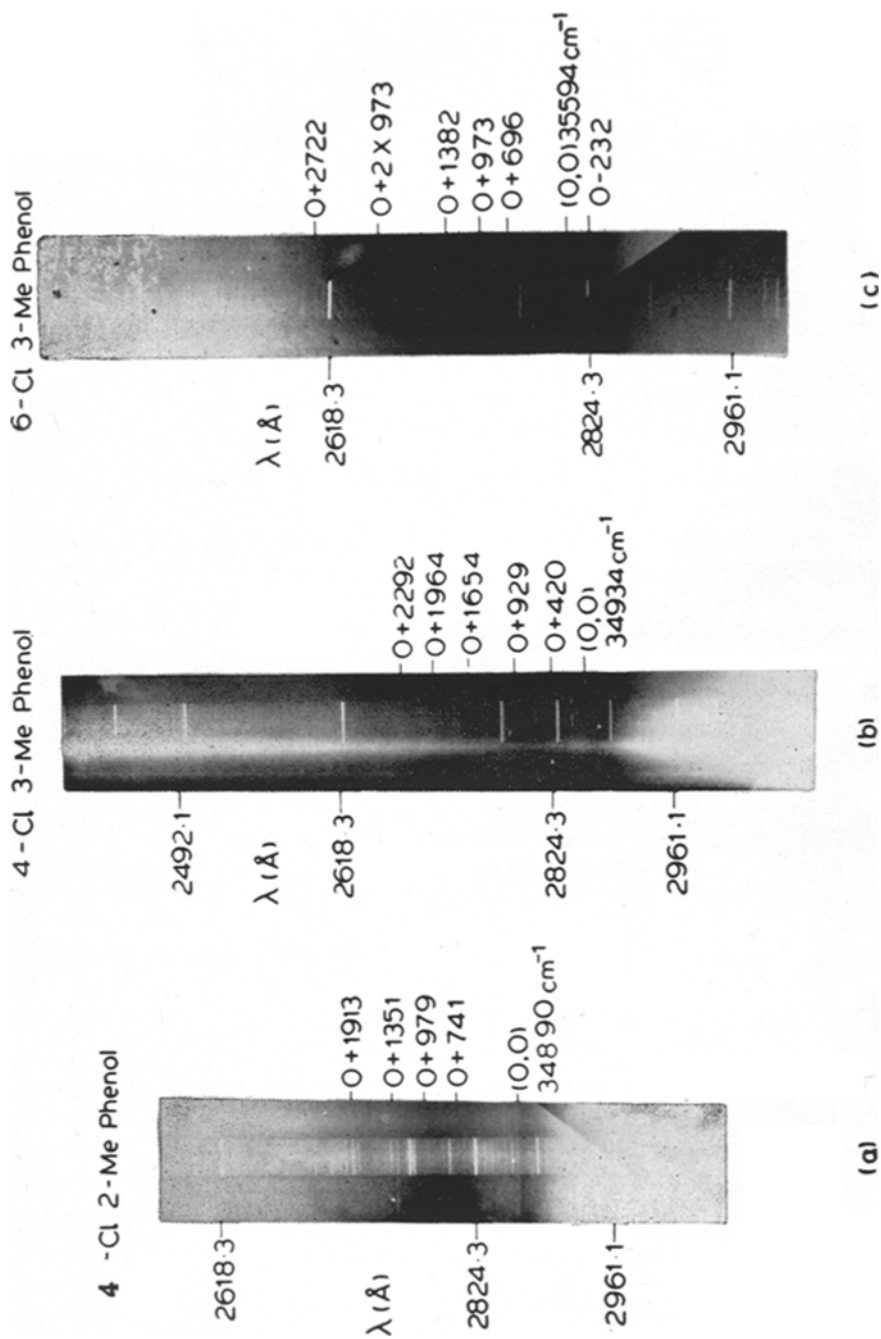


Figure 2. UV absorption spectra of 4-Cl-2-Me, 4-Cl-3-Me and 6-Cl-3-Me phenols.

The ring breathing vibration in the excited state has the magnitude 979 cm^{-1} in 4-Cl 2-Me, 929 cm^{-1} in 4-Cl 3-Me and 973 cm^{-1} in 6-Cl 3-Me phenol and is characterised by the observation of bands involving second quanta of this vibration. It also appears in combination with other prominent vibrations.

Another prominent excited state vibration is observed at 1357 cm^{-1} for 4-Cl 2-Me, at 1367 cm^{-1} for 4-Cl 3-Me and at 1382 cm^{-1} for 6-Cl 3-Me phenol. This is correlated with the respective ground state frequency observed in infrared spectrum at 1400 cm^{-1} , 1410 cm^{-1} and 1410 cm^{-1} and is assigned to a (C-C) stretching mode.

In addition to these fundamental vibrations difference bands involving the frequencies -69 , 75 and 105 cm^{-1} for 4-Cl 2-Me, -94 and 88 cm^{-1} for 4-Cl 3-Me and -77 and 82 cm^{-1} for 6-Cl 3-Me phenols have also been observed. It is not possible at this stage to correlate these difference frequencies to specific fundamentals.

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References

- Bellamy L J 1964 *Infrared spectra of complex molecules* (London: Methuen and Co.)
 Bellamy L J and Davis M J 1948 *Chem. Phys.* **34** 267
 Cave W T and Thompson H W 1950 *Disc. Farad. Soc.* **9** 350
 Green J H S 1962 *Spectrochim. Acta* **18** 39
 Green J H S and Harrison D J 1971 *Spectrochim. Acta* **A27** 793
 Mecke R and Rassmy Z 1955 *Electrochem.* **59** 866
 Randle R R and Whiffen D H 1955 *Proceedings of Symposium on Molecular Spectra, Institute of Petroleum, London*
 Rao C N R 1963 *Chemical applications of infrared spectroscopy* (New York: Academic Press) p. 309
 Rao P Rama Koteswara 1962 *Proc. Indian Acad. Sci.* **A55** 232
 Sanyal N K and Pandey A N 1973 *Indian J. Pure Appl. Phys.* **11** 913
 Sharma S N and Dwivedi C P D 1976 *Indian J. Phys.* **50** 25
 Varsanyi G 1969 *Vibrational spectra of benzene derivatives* (New York: Academic Press)

Footnotes

s = strong, vs = very strong, vvs = very very strong, w = weak, vw = very weak, vvw = very very weak.

ν = Stretching.

β = in-plane bending.

γ = Out-of-plane bending.

ν_s = Symmetric stretching vibration of the groups.

ν_{as} = Asymmetric stretching vibration of the groups.

δ_s = Symmetric bending vibration of CH_2 group.

δ_{as}^+ = Asymmetric bending vibration of CH_2 group.

δ_{as}^- = Asymmetric bending vibration of CH_2 group.

ϕ = in-plane bending of the ring.

δ = Out-of-plane of the ring.