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VIBRATIONAL SPECTRA AND THERMODYNAMIC FUNCTIONS OF THE THREE ISOMERIC METHOXYPHENOLS

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ABSTRACT

Infrared absorption spectra in the range of $250\text{--}4000\text{ cm}^{-1}$ of the three isomeric methoxyphenols are reported. The para methoxyphenol is in the solid phase at room temperature and its spectrum has been investigated in the range of $700\text{--}4000\text{ cm}^{-1}$ in chloroform solution in addition to the spectrum recorded for its nujol mull. Under the usual approximation of the two substituent groups taken as point masses the observed bands have been assigned to different modes of vibration. These assignments have been used to calculate the molar thermodynamic functions for these compounds.

Introduction

The vibrational and electronic spectra of a large number of substituted anisoles and phenols have been reported in the literature [1-6]. The spectroscopic studies of molecules containing both methoxy and hydroxy groups in different positions in the benzene ring are, however, very limited. A short communication on the electronic spectra of methoxyphenols has been made by Suryanarayan and Rao [7-8] and Sen [9] has reported the ultraviolet absorption spectrum of *o*-methoxyphenol in different phases. The Raman spectra of the three isomeric methoxyphenols have been studied by Reitz and Ypsilanti [10]. As a part of the programme to study the spectra of substituted benzenes, we have undertaken the study of the vibrational and electronic spectra of substituted phenols. The vibrational spectra and complete assignments for the three isomeric aminophenols have been reported recently by Verma and Rai [11]. The complete vibrational assignments of the three isomeric methoxyphenols are here reported and the fundamental frequencies observed in these studies have been used to calculate the molar thermodynamic functions of the three isomeric methoxyphenols assuming them to be rigid rotators and harmonic oscillators.

Experimental

Pure samples of the three isomeric methoxyphenols used for recording the spectra were obtained from BDH Chemicals. The liquid samples were

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redistilled under reduced pressure and the solid one was recrystallized before use. The infrared spectra of *o*- and *m*-methoxyphenols which are liquid at room temperature were recorded in pure liquid form while the spectrum of *p*-methoxyphenol which is solid at room temperature was recorded in a nujol mull. A Perkin-Elmer Grating Spectrophotometer Model 521 equipped with CsBr optics was employed to record the spectra in the 250-4000 cm^{-1} frequency range. To distinguish the methyl group vibrations from the nujol vibrations appearing in the same region the infrared spectrum of *p*-methoxyphenol was also recorded in the form of a liquid solution in chloroform on a 13U Perkin-Elmer Double Beam Spectrophotometer in the range of 700-4000 cm^{-1} . The accuracy of the P.E. Grating Spectrophotometer is believed to be $\pm 1 \text{ cm}^{-1}$ throughout the entire region while that of the 13U P.E. Spectrophotometer varies from ± 4 to 15 cm^{-1} . The spectra are reproduced in Figs. 1-3.

Results and Discussion

Assuming OH and OCH_3 groups to behave as point masses, the 30 benzene-like vibrations of *o*- and *m*-methoxyphenols may be classified under C_s symmetry whereas the similar vibrations of the *p*-methoxyphenol may be classified under C_{2v} symmetry. In addition to these vibrations there would be three more vibrations due to the hydroxyl group and 12 vibrations due to the methoxy group, making a total of 45 normal modes of vibrations for the actual molecules. The recommendations of the Joint Commission for Spectroscopy [12] have been followed in the choice of axes for the C_{2v} point group, i. e., the x-axis has been taken perpendicular to the plane of the molecule and the z-axis is colinear with the C_2 axis. The relevant selection rules for infrared and Raman Spectra show that vibrations belonging to all symmetry types may appear in the Raman spectrum and all except those belonging to a_2 symmetry are active in the infrared. The observed vibrational frequencies as well as their assignments to different modes of vibration are given in Tables I-III along with the available Raman data.

In assigning the fundamental frequencies to different modes of vibrations, considerable help has been obtained from the analysis of the vibrational spectra of anisole [1, 2, 4] phenol [3], *p*-cresol [13], methoxybenzaldehydes [14] and *p*-bromoanisole [15]. Since no polarization measurement results for the Raman lines are available intensities and positions of the bands were the main criteria for the assignment. The observation made by Jakobsen and Brewer [5] that only 21 of the 30 benzene-like vibrations of disubstituted benzenes remain unaffected by the nature or the mass of the substituent, has also been taken into account.

Phenyl ring vibrations

The four benzene stretching modes, namely those belonging to e_{2g} (1596 cm^{-1}), e_{1u} (1485 cm^{-1}), b_{2u} (1310 cm^{-1}) and a_{1g} (992 cm^{-1}) give rise to six ring stretching modes in substituted benzenes where the symmetry is lowered sufficiently to remove the degeneracy of the first two modes. The magnitude of the frequency which corresponds to the a_{1g} (992 cm^{-1})

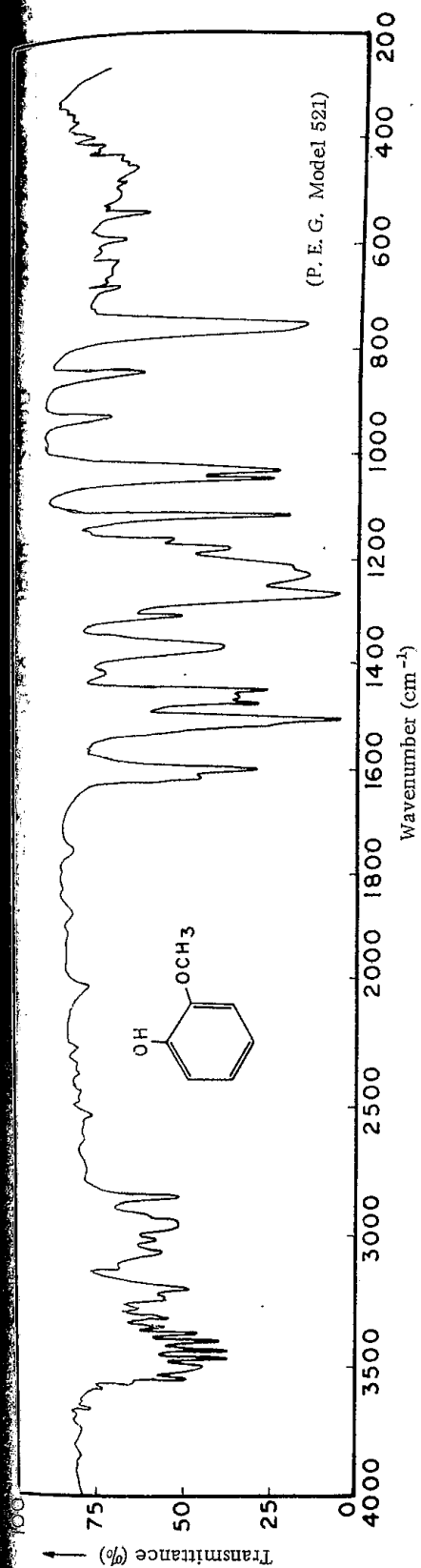


FIG. 1. Infrared absorption spectrum of o-methoxyphenol (liquid phase)

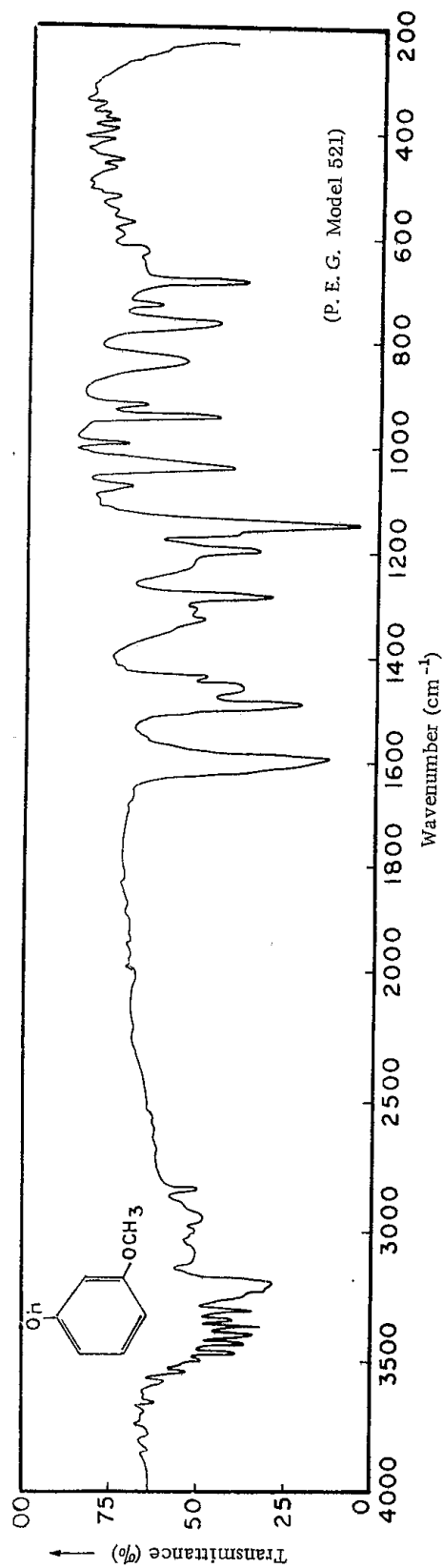


FIG. 2. Infrared absorption spectrum of m-methoxyphenol (liquid phase)

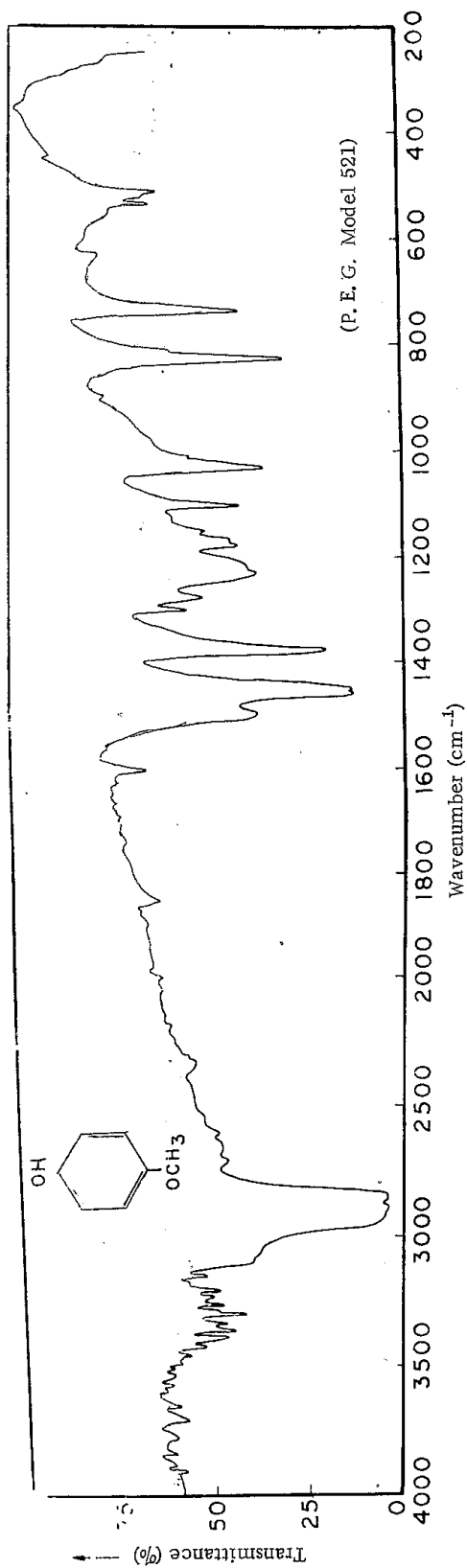


FIG. 3a. Infrared absorption spectrum of p-methoxyphenol (nujol)

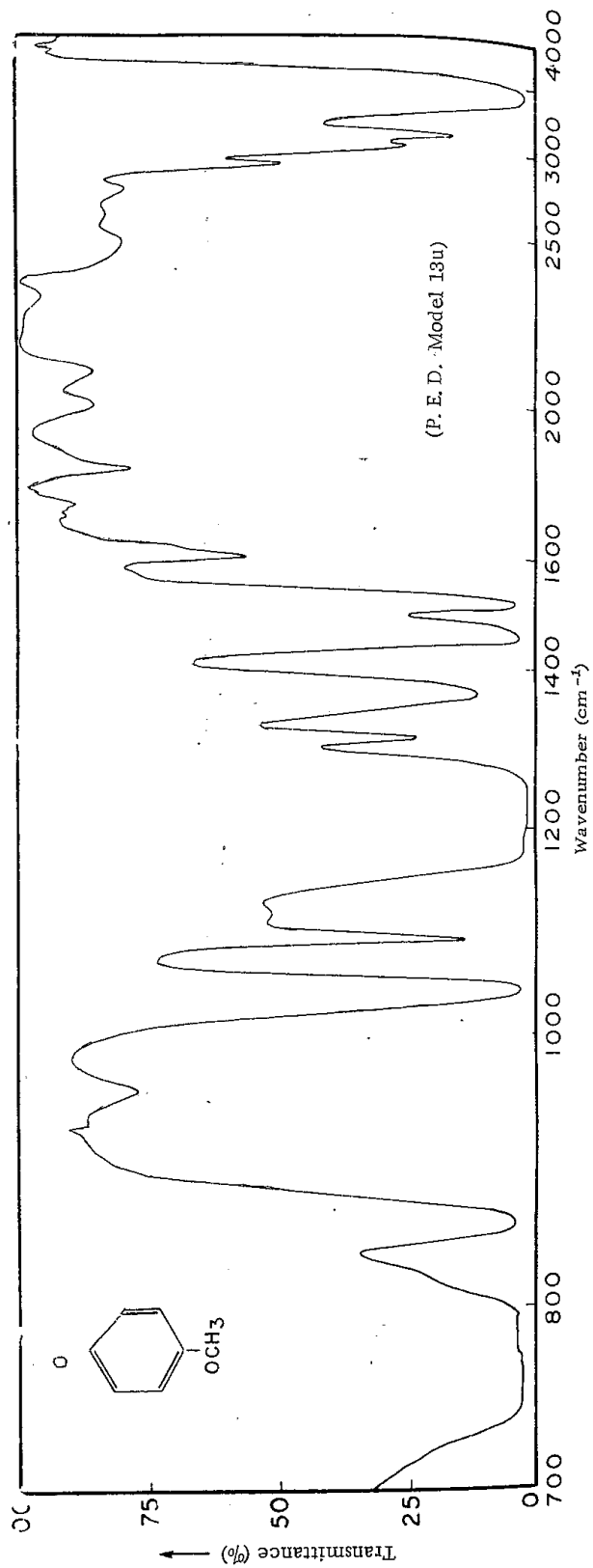


FIG. 3b. Infrared absorption spectrum of p-methoxyphenol (chloroform solution)

TABLE I. Vibrational frequencies and their assignments for o-Methoxyphenol

Raman frequencies (cm ⁻¹) Reitz and Ypsilanti [10]	Infrared frequencies (cm ⁻¹) (liquid)	Assignments
184 (7b)		a" C-OCH ₃ bending o. p.
237 (3b)		a" OH sensitive
308 (5)	308 (sh)	a" O-H bending o. p.
349 (4)	351 (1)	a' C-O-C bending i. p.
	388 (2)	a" C-C-C- bending i. p.
	400 (2)	
	422 (1)	A' 184 + 237 = 421
458 (3)	460 (3)	a" OH sensitive
492 (3)	490 (1)	a' OH sensitive
536 (6)	536 (2)	a' OH sensitive
	548 (4)	a' C-OCH ₃ bending i. p.
583 (5)	592 (3)	a' C-C-C- bending i. p.
	656 (1)	A" 308 + 351 = 659
	672 (1)	a" C-H bending o. p.
	681 (3)	a" O-H bending o. p.
	704 (sh)	a" C-C-C ring def. o. p.
726 (2)	724 (sh)	a" CH ₃ wagging
759 (14)	754 (10)	a' O-CH ₃ bending i. p.
832 (5)	832 (sh)	a' C-C ring breathing
	848 (4)	a" C-H bending o. p.
	933 (3)	a" C-H bending o. p.
	978 (1)	a" C-H bending o. p.
	998 (sh)	a' C-C-C trigonal bending
1028 (3)	1031 (10)	a' CH ₃ rocking
1042 (6)	1047 (10)	a' C-H bending i. p.
	1120 (9)	A' (C-O) stret. + (O-H) i. p.
		bending
1159 (8)	1164 (5)	a' O-CH ₃ stret.
	1180 (7)	a' C-H bending i. p.
1204 (2)	1212 (sh)	a' C-H bending i. p.
	1229 (9)	A' (C-O) stret. + (O-H) i. p.
		bending
1260 (9)	1268 (10)	a' C-OCH ₃ stret.
1302 (4)	1312 (6)	a' C-H bending i. p.
1354 (3b)	1368 (6)	a' CH ₃ sym. def.
	1420 (2)	A" 754 + 672 = 1426
1456 (5b)	1454 (8)	a' CH ₃ asym. def.
	1468 (7)	a' C-C stret.
	1478 (8)	a' CH ₃ asym. def.
1499 (3)	1508 (10)	a' C-C stret.
	1564 (1)	a' C-C stret.
1600 (9b)	1607 (7)	a' C-C stret.
	1615 (sh)	A' 681 + 933 = 1614
1754 (2)	1754 (2)	A' 754 + 998 = 1752
	1798 (1)	A' 490 + 1312 = 1802
	1824 (1)	A' 351 + 1468 = 1819
	1877 (2)	A' 832 + 1047 = 1879
	1992 (1)	A' 490 + 1508 = 1998
	2026 (2)	A" 848 + 1180 = 2028
	2269 (2)	A' 672 + 1600 = 2272
	2362 (1)	A' 1047 + 1312 = 2359
	2439 (1)	A" 933 + 1508 = 2441
	2480 (1)	A' 1212 + 1268 = 2480
	2523 (1)	A' 1212 + 1312 = 2524
	2629 (1)	A' 1031 + 1600 = 2631

TABLE I. (Continued)

Raman frequencies (cm^{-1}) Reitz and Ypsilanti [10]	Infrared frequencies (cm^{-1}) (liquid)	Assignments
2842 (4)	2846 (5)	a' C-H sym. stret. in methyl group
2932 (2b)	2936 (5b)	a' C-H asym. stret. in methyl group
3023 (2)	3008 (4)	a' C-H stret. (Aromatic)
3071 (9b)	3059 (4)	a' C-H stret. (Aromatic)
	3275 (4)	A" $848 + 2 \times 1212 = 3272$
	3290 (3)	A' $351 + 2 \times 1468 = 3287$
	3310 (3)	A" $184 + 2 \times 1564 = 3312$
	3330 (2)	A" $388 + 2 \times 1468 = 3324$
	3341 (4)	A' $978 + 2 \times 1180 = 3338$
	3354 (4)	A" $724 + 2 \times 1312 = 3348$
	3370 (5)	a' O-H stret. (Polymeric)
	3394 (5)	A" $460 + 2 \times 1468 = 3396$
	3401 (6)	A" $978 + 2 \times 1212 = 3402$
	3441 (6)	A" $237 + 2 \times 1600 = 3437$
	3472 (6)	A' $351 + 2 \times 1564 = 3479$
	3500 (3)	A' $592 + 2 \times 1454 = 3498$
	3524 (3)	A' $2 \times 1180 + 1164 = 3524$
3544 (0)	3542 (3)	a' O-H stret. (Monomeric)
	3571 (3)	A" $672 + 2 \times 1454 = 3578$
	3581 (2)	A' $1047 + 2 \times 1268 = 3583$
	3626 (2)	A' $490 + 2 \times 1564 = 3618$
	3636 (2)	A" $704 + 2 \times 1468 = 3640$
	3665 (2)	A" $724 + 2 \times 1468 = 3660$
	3846 (1)	A" $724 + 2 \times 1564 = 3852$
	3878 (1)	A' $460 + 490 + 2 \times 1468 = 3886$
	3909 (1)	A' $998 + 2 \times 1454 = 3904$

The corresponding intensity is given in the parentheses. i. p. = in-plane; o. p. = out-of-plane; sym. = symmetric; asym. = asymmetric; sh = shoulder; def. = deformation; stret. = stretching and b = broad.

frequency of benzene is still a subject of controversy in literature. Wilmschurt and Bernstein [16] have assigned this mode at 725 cm^{-1} and 704 cm^{-1} respectively in the case of *m*-xylene and *m*-xylene- α - α' - d_6 . The lowering was explained by them as due to the interaction between the C-CH₃ stretching vibration and the ring vibration. We have assigned the corresponding mode for *o*-, *m*- and *p*-methoxyphenols to the frequencies 832, 840 and 830 cm^{-1} respectively. The frequency corresponding to the b_{2u} (1310) mode of benzene could not be assigned unambiguously as the spectrum in this region is complicated by the presence of frequencies due to the CH₃ symmetric deformation mode as well as the OH in-plane bending mode. Out of the two components in which the e_{2g} (1596 cm^{-1}) and e_{1u} (1485 cm^{-1}) fundamentals of benzene are split one has a magnitude slightly greater than the corresponding value in benzene whereas the other component has a considerably lower magnitude. These modes have been assigned to the bands at 1607, 1564, 1508, 1468 cm^{-1} in *ortho*-, 1592, 1552, 1490, 1460 cm^{-1} in *meta*- and 1608, 1569, 1508, 1462 cm^{-1} in *para*-methoxyphenol respectively. The four C-H stretching vibrations for disubstituted benzenes usually appear in the frequency range $3000\text{--}3100 \text{ cm}^{-1}$.

TABLE II. Vibrational frequencies and their assignments for m-Methoxyphenol

Raman frequencies (cm^{-1}) Reitz and Ypsilanti [10]	Infrared frequencies (cm^{-1}) (liquid)	Assignments
237 (2)	349 (2)	a" OH sensitive
	395 (2)	a' C-O-C bending i. p.
	454 (2)	a" OH sensitive
472 (00)	469 (2)	a" OH sensitive
	517 (2)	a' OH sensitive
520 (0)	522 (2)	a' OH sensitive
	573 (2)	a' C-OCH ₃ bending i. p.
	588 (2)	A" 349 + 237 = 586
616 (00)	599 (2)	a' C-C-C bending i. p.
	669 (3)	a" C-H bending o. p.
	685 (6)	a" O-H bending o. p.
727 (3)	731 (3)	a" CH ₃ wagging
	764 (5)	a' O-CH ₃ bending i. p.
	840 (4)	a' C-C ring breathing
	845 (sh)	a" C-H bending o. p.
	922 (3)	a" C-H bending o. p.
	943 (5)	a" C-H bending o. p.
989 (5)	995 (2)	a' C-C-C trigonal bending
	1039 (5)	a' CH ₃ rocking
1079 (0)	1075 (2)	a' C-H bending i. p.
1156 (0)	1149 (10)	A' (C-O) stret. + (O-H) bending i. p.
	1166 (sh)	a' O-CH ₃ stret.
	1196 (6)	a' C-H bending i. p.
	1225 (sh,b)	A' (C-O) stret. + (O-H) bending i. p.
1283 (1)	1285 (6)	a' C-OCH ₃ stret.
	1310 (1)	a' C-H bending i. p.
	1329 (2)	a' CH ₃ sym. def. in methyl group
1445 (0)	1443 (4)	a' CH ₃ asym. def. in methyl group
	1460 (6)	a' C-C stret.
	1490 (6)	a' C-C stret.
	1552 (sh)	a' C-C stret.
1601 (2b)	1592 (9)	a' C-C stret.
	1873 (1)	A' 840 + 1039 = 1879
	1938 (1)	A" 943 + 995 = 1938
	1990 (1)	A' 2 x 995 = 1990
	2232 (1)	A' 2 x 517 + 1196 = 2230
	2292 (1)	A' 2 x 349 + 1592 = 2290
	2460 (1)	A' 2 x 573 + 1310 = 2456
	2598 (1)	A' 2 x 522 + 1552 = 2596
	2836 (3)	a' C-H sym. stret. in methyl group
	2950 (3)	a' C-H asym. stret. in methyl group
	3000 (2)	a' C-H stret. (Aromatic)
	3028 (2)	a' C-H stret. (Aromatic)
3092 (0)	3088 (2b)	a' C-H stret. (Aromatic)
	3150 (2)	

TABLE II. (Continued)

Raman frequencies (cm^{-1}) Reitz and Ypsilanti [10]	Infrared frequencies (cm^{-1}) (liquid)	Assignments
	3192 (4)	A' $2 \times 1592 = 3184$
	3225 (4)	A' $3 \times 1075 = 3225$
	3269 (2)	A' $1285 + 2 \times 995 = 3275$
	3320 (2)	A' $349 + 2 \times 1490 = 3329$
	3334 (3)	A" $943 + 2 \times 1196 = 3335$
	3345 (3)	A" $237 + 2 \times 1552 = 3341$
	3362 (4)	a' O-H stret. (Polymeric)
	3386 (3)	A" $469 + 2 \times 1460 = 3389$
	3430 (2)	A' $517 + 2 \times 1460 = 3437$
	3460 (2)	A' $349 + 2 \times 1552 = 3452$
	3536 (2)	a' O-H stret. (Monomeric)
	3556 (1)	A" $669 + 2 \times 1443 = 3552$
	3579 (1)	A" $922 + 2 \times 1329 = 3580$
	3619 (1)	A' $517 + 2 \times 1552 = 3621$
	3657 (1)	A" $731 + 2 \times 1460 = 3651$
	3690 (1)	A' $1075 + 2 \times 1310 = 3695$
	3793 (1)	A' $1166 + 2 \times 1310 = 3786$
	3840 (1)	A" $731 + 2 \times 1552 = 3835$
	3880 (1)	A' $1310 + 2 \times 1285 = 3880$
	3903 (1)	A" $922 + 2 \times 1490 = 3902$
	3930 (1)	A' $828 + 2 \times 1552 = 3932$

Similar results have been obtained in the present investigation and since this region is comparatively free from complicating features, the assignments are straightforward. These are given in the tables. The C-H in-plane bending modes and C-H out-of-plane bending modes of vibrations appear in the range of $1000\text{--}1350\text{ cm}^{-1}$ and $650\text{--}1000\text{ cm}^{-1}$ respectively. The C-H in-plane bending modes arise from a_{2g} (1340 cm^{-1}), e_{2g} (1178 cm^{-1}), b_{2u} (1152 cm^{-1}) and e_{1u} (1037 cm^{-1}) modes of benzene. Bands observed at $1312, 1212, 1180, 1047\text{ cm}^{-1}$ for *ortho*-, at $1310, 1196, 1075\text{ cm}^{-1}$ for *meta*- and at $1301, 1219, 1180$ and 1012 cm^{-1} for *para*-methoxyphenols have been ascribed to this mode. The C-H out of plane bending modes derived from b_{2u} (995 cm^{-1}), e_{2u} (975 cm^{-1}), e_{2g} (850 cm^{-1}) and a_{2u} (673 cm^{-1}) modes of benzene are identified at $978, 933, 848, 672\text{ cm}^{-1}$ for *ortho*- and $943, 922, 845, 669\text{ cm}^{-1}$ for *meta*-methoxyphenols. In the case of p-methoxyphenol only three bands ascribed to these modes are observed at $982, 925$ and 656 cm^{-1} . Two in-plane and two out of plane C-H bending vibrations become C-substituent vibrations in disubstituted benzenes and have been discussed along with the substituent vibrations.

OH group vibrations

In principle the three vibrations of the OH group could be assigned easily by analogy to the vibrational assignments of the OH modes in phenol,

TABLE III. Vibrational frequencies and their assignments for p-methoxyphenol

Raman frequencies (cm^{-1}) Reitz and Ypsilanti [10]	Infrared frequencies (cm^{-1})		Assignments
	(Nujol)	(CHCl_3)	
252 ($\frac{1}{2}$)	329 (1)		b_1 OH sensitive
371 (4)	368 (1)		b_1 OH sensitive
391 ($\frac{1}{2}$)	389 (1)		a_1 C-O-C bending i. p.
439 (2)	442 (2)		b_1 C-C-C bending o. p.
522 (1)	518 (6)		b_1 OH sensitive
	537 (6)		b_1 OH sensitive
	557 (4)		b_2 C-OCH ₃ bending i. p.
	596' (1)		b_2 C-C-C bending i. p.
640 (4)	642 (1)		b_1 O-H bending o. p.
	656 (1)		b_1 C-H bending o. p.
703 (3)	706 (sh)		b_1 CH ₃ wagging
	741 (9)		a_1 O-CH ₃ bending i. p.
	814 (4)		A_1 368 + 442 = 810
830 (8)	830 (9)	825 (10)	a_1 C-C ring breathing
847 (8)			a_2 C-H bending o. p.
	925 (sh)	928 (2)	b_1 C-H bending o. p.
	982 (2)		b_1 C-H bending o. p.
	997 (sh)		a_1 C-C-C trigonal bending
	1012 (4)		a_1 C-H bending i. p.
1026 ($\frac{1}{2}$)	1030 (9)	1032 (10)	b_2 CH ₃ rocking
	1106 (8)	1100 (9)	A_1 (C-O) stret. + (O-H)
			bending i. p.
1166 (4b)	1159 (4)		a_1 O-CH ₃ stret.
	1180 (8)		b_1 C-H bending i. p.
	1219 (sh)		b_2 C-H bending i. p.
	1232 (9)	1226 (10b)	A_1 (C-O) stret. + (O-H)
			bending i. p.
1274 (5b)	1276 (7)		a_1 C-OCH ₃ stret.
	1301 (6)	1298 (6)	b_2 C-H bending i. p.
	1349 (sh)	1351 (8)	a_1 CH ₃ sym. def. in methyl
			group
1452 (2b)	1452 (10)	1451 (10)	b_2 CH ₃ asym. def. in methyl
			group
	1462 (10)		b_2 C-C stret.
	1508 (6)	1510 (10)	a_1 C-C stret.
	1569 (1)		b_2 C-C stret.
1613 (5b)	1608 (3)		a_1 C-C stret.
	1632 (1)		A_1 2 \times 814 = 1628
	1670 (1)		B_1 2 \times 518 + 642 = 1678
	1700 (1)		B_1 2 \times 389 + 925 = 1703
	1714 (1)	1710 (1)	B_1 2 \times 368 + 982 = 1718
	1734 (1)	1734 (1)	A_2 2 \times 442 + 847 = 1731
	1753 (1)		B_1 2 \times 557 + 642 = 1756
	1856 (3)	1857 (2)	B_2 1030 + 830 = 1860
	1879 (1)		A_2 2 \times 518 + 847 = 1883
	1905 (1)		A_1 2 \times 368 + 1159 = 1895
	2000 (1)	2000 (3)	B_1 2 \times 537 + 925 = 1999
	2047 (1)		A_1 2 \times 518 + 1012 = 2048
	2189 (1)		B_2 2 \times 576 + 1030 = 2180
	2239 (1)		A_1 2 \times 537 + 1159 = 2233

TABLE III. (Continued)

Raman frequencies (cm^{-1}) Reitz and Ypsilanti [10]	Infrared frequencies (cm^{-1})		Assignments
	(Nujol)	(CHCl_3)	
	2293 (1)	2284 (2)	$B_1 \ 2 \times 656 + 982 = 2294$
	2328 (2)		$B_2 \ 2 \times 557 + 1219 = 2333$
	2354 (2)		$B_1 \ 656 + 2 \times 847 = 2350$
	2468 (1)	2470 (2)	$A_1 \ 2 \times 656 + 1159 = 2477$
	2612 (2)		$B_2 \ 2 \times 656 + 1301 = 2613$
	2673 (1)		$A_1 \ 2 \times 830 + 1012 = 2672$
	2713 (2)	2730 (2)	$A_1 \ 2 \times 706 + 1301 = 2713$
2835 (2)	2838 (10)	2840 (5)	a_1 C-H sym. stret. in methyl group
2951 (0)	2943 (10)	2960 (7)	b_2 C-H asym. stret. in methyl group
3007 ($\frac{1}{2}$)	3007 (sh)		b_2 C-H stret. (Aromatic)
	3042 (sh)		b_2 C-H stret. (Aromatic)
3069 (5b)	3070 (sh)	3065 (8)	a_1 C-H stret. (Aromatic)
	3142 (3)		$B_2 \ 706 + 2 \times 1219 = 3144$
	3181 (2)		$B_2 \ 1569 + 1608 = 3177$
	3205 (4)		$A_1 \ 741 + 2 \times 1232 = 3205$
	3223 (3)		$A_1 \ 2 \times 1608 = 3216$
	3234 (3)		a_1 O-H stret. (Polymeric)
	3260 (4)		$B_1 \ 656 + 2 \times 1301 = 3258$
	3283 (4)		$A_1 \ 814 + 2 \times 1232 = 3278$
	3299 (5)		$A_1 \ 368 + 2 \times 1462 = 3292$
	3331 (3)		$A_1 \ 997 + 2 \times 1159 = 3323$
	3354 (4)		$A_1 \ 997 + 2 \times 1180 = 3357$
	3417 (3)	3415 (10)	a_1 O-H stret. (Monomeric)
	3457 (2)		$B_1 \ 537 + 2 \times 1462 = 3461$
	3489 (2)		$B_2 \ 1030 + 2 \times 1232 = 3494$
	3565 (1)		$B_2 \ 557 + 2 \times 1604 = 3565$
	3610 (1)		$B_1 \ 706 + 2 \times 1452 = 3610$
	3626 (1)		$B_2 \ 1030 + 2 \times 1301 = 3632$
	3642 (2)		$B_1 \ 1180 + 2 \times 1232 = 3644$
	3768 (1)	3760 (1)	$B_2 \ 1462 + 2 \times 1159 = 3772$
	3778 (1)		$B_2 \ 557 + 2 \times 1608 = 3773$
	3833 (2)		$B_1 \ 925 + 2 \times 1452 = 3829$
	3887 (1)		$B_1 \ 982 + 2 \times 1452 = 3886$

TABLE IV. Moments of inertia in 10^{-40} gm cm^2 for the three isomeric methoxyphenols

Moments of inertia	o-Methoxyphenol	m-Methoxyphenol	p-Methoxyphenol
I_x	1119.714	1119.714	877.359
I_y	354.901	354.901	140.395
I_z	764.813	764.813	736.964

phenol -d₅ and phenol -OD. However, the presence of monomeric and polymeric OH vibrations complicate the assignment somewhat. In the present investigation the bands observed at 3542 and 3370 cm⁻¹ for *ortho*-, 3536 and 3362 cm⁻¹ for *meta*- and 3417 and 3234 cm⁻¹ for *para*-methoxyphenols have been assigned as due to the monomeric and polymeric OH stretching vibrations respectively. In the associated molecules, Davies [17] assigned a broad band in the region 600-700 cm⁻¹ to the OH out of plane bending mode. Evans has assigned the band at ~ 650 cm⁻¹ and ~ 300 cm⁻¹ to the monomeric and polymeric OH out of plane bending modes respectively in phenol. In the present investigation we have identified these corresponding modes at 681,308 cm⁻¹ in *ortho*- and at 642,329 cm⁻¹ in *para*-methoxyphenol. However, in the case of *meta*-methoxyphenol only one band due to the monomeric OH out of plane bending mode could be observed at 685 cm⁻¹.

The C-O stretching mode [18] occurs in the range 1030-1200 cm⁻¹ and interacts with the OH in plane bending mode. The resulting vibrations are observed at 1120, 1229 cm⁻¹ in *ortho*-, 1149, 1225 cm⁻¹ in *meta*- and 1106, 1232 cm⁻¹ in the *para*-isomer respectively. This is in accordance with a similar assignment by Hadzi and Sheppard [19]. In phenol Evans has attributed six modes as substituent sensitive. In the present case also six OH sensitive vibrations are obtained, two of them have been discussed earlier as the C-O stretching mode and the OH in plane bending mode. The other OH sensitive modes are observed at 536, 490, 460 and 237 cm⁻¹ for *ortho*-, at 522, 517, 454 and 237 cm⁻¹ for *meta*- and at 537, 518, 442 and 252 cm⁻¹ for *para*-methoxyphenols respectively. Out of these the 490 and 237 cm⁻¹ frequencies of *ortho*- 517 and 237 cm⁻¹ bands of *meta*- and 518 and 252 cm⁻¹ frequencies of the *para*-isomer may be assigned as substituent sensitive ring vibrations. These are single component each of the 606 cm⁻¹ and 404 cm⁻¹ vibrations of benzene. The remaining two vibrations may then be attributed to the C-OH in plane and out of plane bending modes.

OCH₃ group vibrations

The strong band observed at 1268, 1285 and 1276 cm⁻¹ respectively for *o*-, *m*- and *p*-methoxyphenol has been assigned to the C-OCH₃ stretching mode. This mode of vibration has been identified at 1242, 1268 and 1255 cm⁻¹ in *o*-, *m*- and *p*-methoxybenzaldehyde [14]. The C-OCH₃ in plane bending mode could be identified in bands observed at 548, 573 and 557 cm⁻¹ for *o*-, *m*- and *p*-methoxyphenol respectively. But in the present investigation no bands ascribable to C-OCH₃ out of plane mode is observed in the infrared spectra. Bands arising from the OCH₃ stretching mode have been reported in the literature near 1150 cm⁻¹. We have assigned this mode to bands observed at 1164, 1166 and 1159 cm⁻¹ for *o*-, *m*- and *p*-methoxyphenols respectively. The O-CH₃ in plane bending mode has been observed in the case of *o*-, *m*- and *p*-methoxyphenols at 754, 764 and 741 cm⁻¹ respectively.

Fox and Martin [20] examined a large number of hydrocarbons containing methyl group and assigned two strong bands observed in the neighbourhood of 2962 and 2872 cm⁻¹ to the C-H asymmetric and symmetric stretching modes, respectively of in the methyl group. The bands observed at 2936 and 2846 cm⁻¹; 2950 and 2836 cm⁻¹ and 2943 and 2838 cm⁻¹ in the spectrum of *o*-, *m*- and *p*-methoxyphenol respectively have been assigned to these

TABLE V. Thermodynamic functions (in cal/Mole/°K) of the three isomeric methoxyphenols for the ideal gas state

T_{O_K}	C_v^{O}	$(H^{\text{O}} - E_0^{\text{O}})/T$	$-(G^{\text{O}} - E_0^{\text{O}})/T$	S^{O}
o-Methoxyphenol				
100	9.34	8.84	53.48	62.32
200	18.82	12.35	60.59	72.94
298.16	29.04	17.48	66.27	83.75
300	29.22	17.72	66.35	84.07
400	38.44	21.68	71.86	93.55
500	44.14	27.08	77.27	104.35
600	51.70	30.44	82.50	112.93
700	55.90	34.02	87.37	121.39
800	59.20	37.21	92.16	129.37
900	61.78	40.05	96.66	136.71
1000	63.70	42.62	101.24	143.86
1100	65.10	44.67	105.17	149.85
1200	66.29	46.52	109.13	155.65
1300	67.27	48.25	112.97	161.22
1400	68.04	49.76	116.52	166.28
1500	68.72	51.17	120.12	171.29
m-Methoxyphenol				
100	7.57	8.31	53.30	61.61
200	15.01	10.66	59.66	70.32
298.16	24.55	14.32	64.48	78.79
300	24.72	14.39	64.55	78.94
400	33.60	18.61	69.26	87.88
500	40.83	22.74	73.86	96.60
600	46.44	26.60	78.38	104.97
700	50.56	29.99	82.68	112.67
800	53.73	33.02	86.94	113.96
900	56.17	35.80	91.06	126.86
1000	58.04	38.10	94.99	133.10
1100	59.48	40.13	98.74	138.87
1200	60.68	41.95	102.27	144.22
1300	61.57	43.58	105.72	149.30
1400	62.33	45.04	109.03	154.07
1500	63.96	46.34	112.14	158.48
p-Methoxyphenol				
100	7.98	8.37	50.73	59.11
200	16.74	11.22	57.29	68.52
298.16	26.61	15.34	62.53	77.87
300	26.76	15.40	62.58	77.99
400	35.78	19.88	67.67	87.57
500	42.97	24.11	72.57	96.69
600	48.51	28.15	77.36	105.51
700	52.67	31.67	81.97	113.64
800	55.81	34.76	86.41	121.16
900	58.22	37.48	90.70	128.18
1000	60.07	37.84	94.73	134.57
1100	61.52	41.93	98.67	140.67
1200	62.66	43.77	102.36	146.13
1300	63.58	45.40	105.97	151.38
1400	64.32	46.87	109.31	156.18
1500	64.97	48.20	112.66	160.87

two modes of vibrations. The CH_3 asymmetric deformation modes have been identified at 1478 and 1454 cm^{-1} in *o*-methoxyphenol. But in the case of *m*- and *p*-isomers only one band at 1443 and 1452 cm^{-1} respectively has been observed. The CH_3 symmetric deformation mode has been assigned at 1368, 1329 and 1349 cm^{-1} respectively for the *o*-, *m*- and *p*-isomers. The frequencies caused by the CH_3 rocking and wagging modes have been found at 1031, 1039, 1030 cm^{-1} and at 724, 731, 706 cm^{-1} in the case of *o*-, *m*- and *p*-methoxyphenol respectively.

Thermodynamic Functions

The thermodynamic functions were calculated for the ideal vapour at one atmosphere pressure in the standard manner [21] using the harmonic oscillator, rigid rotator approximation. The moments of inertia I_x , I_y and I_z along the coordinate axes x , y and z have been calculated considering the molecule as a planar one and the substituent groups as single mass points. The moments of inertia calculated thus are given in Table IV, and the values of C_V^0 (heat capacity), $(H^0 - E_0^0)/T$ (enthalpy function), $(G^0 - E_0^0)/T$ (free energy function) and S^0 (entropy) at various temperatures ranging from 100-1500°K for the three isomeric methoxyphenols are presented in Table V. Here E_0^0 is the energy of one mole of an ideal gas at absolute zero, H^0 is its enthalpy and G^0 is its free energy. No experimental value for these compounds have been available in literature.

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