424. *The Thermodynamic Properties of Organic Oxygen Compounds. Part II.*[1] *Vibrational Assignment and Calculated Thermodynamic Properties of Phenol.*

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A complete vibrational assignment of phenol is correlated with those of *o*-phen[^{2}H]ol, toluene, fluorobenzene, and aniline. The thermodynamic functions are tabulated for phenol in the ideal-gas state from 0° to 1000° K.

THE vibrational spectra of phenol have been measured several times and partial assignments of the fundamentals have been made by Kohlrausch and Wittek [2] from the Raman spectrum and by Mecke and his co-workers [3] from the infrared spectrum. Davies and Jones [4] discussed the infrared spectrum of *o*-phen[^{2}H]ol in relation to that of phenol and considered the modes associated with the hydroxyl group. In the present work a complete vibrational assignment is made from which, in conjunction with molecular structure data, including the barrier height to free rotation of the hydroxyl group,[5] the thermodynamic functions are calculated.

ASSIGNMENT

The spectra are collected in Table 1, where the depolarisation ratios of the Raman lines are those of Kohlrausch and Wittek.[2] As they provide important additional information, the infrared spectra of phenol vapour and of *o*-phen[^{2}H]ol, in carbon disulphide solution and in the solid, are also tabulated. The phenol molecule has approximately C_{2v} symmetry and the fundamental vibrations, exclusive of those associated with the hydroxyl group, divide into $11a_1 + 10b_1 + 3a_2 + 6b_2$. All the species are Raman active, but only those of the a_1 class are polarised, the rest being depolarised, whilst in the infrared the a_1, b_1, and b_2 vibrations can yield approximately type A, B, and C contours, respectively, the a_2 species being inactive. The complete assignment for phenol is given in Table 2, where the approximate description of the modes is that of Whiffen [6] and the numbering is that of Wilson.[7]

The majority of these assignments follow in a straightforward way from those of other

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[1] The paper, Andon, Biddiscombe, Cox, Handley, Harrop, Herington, and Martin, *J.*, 1960, 5246, is to be regarded as Part I.

[2] Kohlrausch and Wittek, *Monatsh.*, 1943, **74**, 1.

[3] (*a*) Mecke and Rossmy, *Z. Elektrochem.*, 1955, **59**, 86; (*b*) Mecke and Greinacher, *ibid.*, 1957, **61**, 530.

[4] Davies and Jones, *J.*, 1954, 120.

[5] Kojima, *J. Phys. Soc. Japan*, 1960, **15**, 284.

[6] Whiffen, *J.*, 1956, 1350; Randle and Whiffen, " Molecular Spectroscopy," Conference held by the Institute of Petroleum, London, 1954.

[7] Wilson, *Phys. Rev.*, 1934, **45**, 706.

TABLE 1. *Vibrational spectra of phenol and* o-*phen*[^{2}H]*ol.*

$C_6H_5{\cdot}OH$				$C_6H_5{\cdot}O^2H$		
Raman (melt)		Infrared		Infrared		
Δν (cm.$^{-1}$)	ρ [a]	Vapour [b]	CCl_4 soln.	CS_2 soln. [c]	Crystal [d]	Assignment
241(s)	0·79					b_2 fundamental
415(vw)		408(4)				b_1 and a_2 fundamentals
507(w)		496(5) 502(6)	502(w)			b_2 fundamental
532(s)	0·72	514(sh) 526(3) 533(sh) }	526(w)			a_1 fundamental
617(s)	0·84	591(1)	617(w)			b_1 fundamental
		681(4) 686(8) 691(4) } *C*	688(s)	690(s)	689(9)	b_2 fundamental
756(s)	[0·60]	742(7) 747(9) 751(7) } *C*	752(s)	750(s)	754(10)	b_2 fundamental
812(s)	0·13	806(sh) 810(5) 814(5) } *A*	810(s)	805(m)	805(9)	a_1 fundamental
828(m)		823(5)	825(m)	—	821(sh)	a_2 fundamental
		828(sh)				
		875(sh) 881(4) 888(sh) } *C*	884(m)	885(m)	879(sh) 887(7)	b_2 fundamental
				910(s)	932(sh)	C–O–D bending fundamental
			958(vw)		961(7)	a_2 fundamental
			978(vw)		976(8)	b_2 fundamental
995(vw)						756 + 240 = 996 (A_1)
1002(s)	0·07	999(1)	1000(m)	1000(m)	995(8)	a_1 fundamental
1014(vw)						507 + 507 = 1014 (A_1)
1024(s)		1015(1) 1026(1) 1033(1) } *A*	1024(m)	1024(w)	1020(sh)	a_1 fundamental
1072(m)		1057(3) 1069(sh) } *B*	1071(m)	1070(m)	1074(9)	b_1 fundamental
			1106(w)		1104(4)	688 + 415 = 1103 (A_2 or B_1)
1152(m)	0·64	1142(sh)	1153(m)	1148(m)	1152(8)	b_1 fundamental
		1148(6)				
1167(5)	0·64	1167(9)	1167(s)	1170(vw)	1166(7)	a_1 fundamental
		1175(10)	1182(s)			C–O–H bending fundamental
		1182(10)				
		1196(sh)				688 + 500 = 1188 (A_1)
			1220(s)	1220(sh)	1223(sh)	408 + 810 = 1218 (A_2 or B_1)
1250(m)		1253(sh) 1259(9) } *A*	1255(s)	1242(s)	1242(9)	a_1 fundamental
					1284(s)	[*530*] + *754* = *1284* (B_2)
				1300(vw)	1300(s)	[*500*] + *805* = *1305* (B_2)
		1310(sh)	1313(w)		1316(3)	b_1 fundamental
		1333(5)	1322(sh)			
		1344(5)	1344(m)	1330(vw)	1332(4)	b_1 fundamental; 502 + 825 = 1327 (B_1)
		1349(5)				823 + 526 = 1349 (A_2)
						810 + 526 = 1336 (A_1)
					1362(5)	[*400*] + *961* = *1361* (A_1 or B_2)
1381(vw)			1384(m)		1383(4)	500 or [500] + 887 = 1387 (A_1)
1466(w)		1460(sh) 1471(sh)	1472(s)	1456(s)	1456(8) 1471(sh)	b_1 fundamental
1498(w)		1492(8) 1497(8) 1506(sh) } *A*	1498(s)		1493(9)	a_1 fundamental
			1527(w)		1520(sh) 1543(2)	526 or [*530*] + 1000 = 1526, [1530] (A_1)
1595(vs)	0·74	1600(9)	1596(s)	1600(s)	1585(9)	a_1 fundamental
1604(vs)	0·74		1604(sh)		1592(sh)	b_1 fundamental
					1634(sh)	*821* + *821* = *1642* (A_1)
			1707(w)	1690(vw)	1698	825 + 884 = 1709 (B_1); *821* + *887* = *1708* (B_1)
			1777	1760(vw)	1761	884 + 884 = 1768 (A_1); 887 + 887 = 1774 (A_1)

TABLE 1. (*Continued.*)

$C_6H_5{\cdot}OH$				$C_6H_5{\cdot}O^2H$		
Raman (melt)		Infrared		Infrared		
$\Delta\nu$ (cm.$^{-1}$)	ρ [a]	Vapour [b]	CCl_4 soln.	CS_2 soln.[c]	Crystal [d]	Assignment
			1810			825 + 978 = 1803 (B_1)
			1842	1840(vw)	1835	884 + 958 = 1842 (B_1); *887 + 961 = 1848* (B_1)
				1920(vw)	1916(4)	*961 + 961 = 1922* (A_1)
			1932(w)		1934(sh)	958 + 978 = 1936 (B_1); *961 + 973 = 1934* (B_1)
			1950(w)			978 + 978 = 1956 (A_1)
				2650(m)	2370	O–D stretching fundamental
3027(0) [a]		3030(5)	3023(sh)			b_1 fundamental
3047(5*b*) [a]			3046(m)			a_1 fundamental
3063(8*b*) [a]						a_1 fundamental
			3076(m)			a_1 fundamental
3085(½) [a]			3091			b_1 fundamental
		3623(6)	3612(m)			O–H stretching fundamental

[a] Depolarisation ratios as given by Kohlrausch and Wittek.[2] [b] Mecke, D.M.S. Catalogue of Infrared Spectra, Butterworths, London, No. 3344. [c] Mecke, D.M.S. Catalogue of Infrared Spectra, Butterworths, London, No. 3690. [d] Mecke and Greinacher, *Z. Elektrochem.*, 1957, **61**, 530. Italicised summations relate to $C_6H_5{\cdot}OD$. [ ] inferred from combination bands.

TABLE 2. *Correlation of the fundamental frequencies* (*cm.*$^{-1}$) *of phenol,* o-*phen*[^{2}H]*ol, toluene, fluorobenzene, and aniline.*

	Mode [6]	No.[7]	Phenol	*o*-Phen[^{2}H]ol	Toluene	Fluorobenzene	Aniline
a_1	ν(CH)	20*a*	3085	—	3067	3084	3073
	ν(CH)	2	3076	—	3056	3053	3050
	ν(CH)	13	3044	—	3003	3040	3058
	ν(CC)	8*a*	1596	1600	1585	1603	1600
	ν(CC)	19*a*	1497	1493	1492	1496	1498
	β(CH)	9*a*	1167	1170	1178	1156	1171
	β(CH)	18*a*	1026	1024	1030	1021	1027
	Ring	1	999	1000	1004	1010	994
	X-sens.	7*a*	1259	1242	1208	1218	1277
	X-sens.	12	810	805	786	807	818
	X-sens.	6*a*	526	[530]	521	519	531
b_1	ν(CH)	20*b*	3091	—	3090	3098	3073 *
	ν(CH)	7*b*	3030	—	3039	3072	3050 *
	ν(CC)	8*b*	1604	1600 *	1604	1596	1600 *
	ν(CC)	19*b*	1465	1456	1455	1459	1464
	ν(CC)	14	1333	1330	1330	1325	1340
	β(CH)	3	1313	1316	1313	1295	1311
	β(CH)	9*a*	1145	1148	1155	1156 *	1154
	β(CH)	15	1071	1070	1081	1066	1054
	α(CCC)	6*b*	617	—	623	615	619
	X-sens.	18*b*	408	~[400]	344	406	388
a_2	γ(CH)	17*a*	958	961	966	955	964
	γ(CH)	10*a*	825	821	843	830	833
	ϕ(CC)	16*a*	408 *	~[400]	407	406 *	415
b_2	γ(CH)	5	978	973	981	980	988
	γ(CH)	17*b*	881	885	895	896	886
	γ(CH)	10*b*	749	750	729	754	758
	ϕ(CC)	4	688	690	695	685	690
	X-sens.	16*b*	500	[500]	464	500	504
	X-sens.	11	241	—	216	242	233
	OH(OD) bending		1180	910			
	OH(OD) stretching		3623	~2650			

* Frequency used twice. (—) Frequency obscured, or not measured. [ ] Inferred from combination bands.

monosubstituted benzenes;[6] as is usual, the essentially CH stretching frequencies ν(CH) are not adequately resolved and the assignments given are rather arbitrary. Above 2000 cm.$^{-1}$ only frequencies assigned as fundamentals are given in Table 1, as several possibilities exist to account for the weak combination bands found in this region. The frequencies in the range 1630—1950 cm.$^{-1}$ are tabulated since their interpretation[8] in terms of the out-of-plane C–H deformation γ(CH) provides support for the assignments made for these modes.

Of the three frequencies arising from the hydroxyl group, one is the O–H stretching frequency, another is essentially the torsion of the group about the C–O bond, and the third is the C–O–H angular deformation, the assignment of which has caused some difficulty in the past. From the work of Davies[4] and of Mecke[3] it follows that the last value can be taken as 1180 cm.$^{-1}$; this absorption disappears on deuteration, and a new band appears at 910 cm.$^{-1}$ in dilute solution. This C–O–D bending fundamental give rise to a broad absorption from 930 to 980 cm.$^{-1}$ in the spectrum of the crystal, in which however the two γ(CH) frequencies at 961 and 973 cm.$^{-1}$ may be distinguished. The other assignments for the deuterated substance follow from those for phenol, and are listed in Table 2 with those for toluene, fluorobenzene, and aniline. In all these compounds the masses of the substituents are almost the same, and the changes in even the X-sensitive mode[6] are fairly small; again the assignments of the ν(CH) frequencies are rather arbitrary.

Of the C–C stretching frequencies ν(CC) only number 14, the lowest in the b_1 class, requires comment. From Mair and Hornig's assignment for benzene, a value near 1310 cm.$^{-1}$ is expected,[6] and in fluorobenzene the assignment at 1320 cm.$^{-1}$ is satisfactory. In phenol, however, there is found a doublet at 1332—1344 cm.$^{-1}$ which is virtually unchanged on deuteration.[4] This doublet may be due to Fermi resonance with the combination $502 + 825 = 1327$ (B_1), and the fundamental is here assigned as 1333 cm.$^{-1}$. In toluene Wilmshurst and Bernstein[9] assigned it as 1155 cm.$^{-1}$; however, they recorded a depolarised Raman line at 1329 cm.$^{-1}$ and in several of the recorded infrared spectra of toluene[10] weak absorption is found at *ca.* 1333 cm.$^{-1}$. In Table 2, therefore, the fundamental has been assigned as 1330 cm.$^{-1}$ in toluene; the same value is given by Kovner and Peregudov.[11] Recently, Fuson, Garrigou-Lagrange, and Josien[12] have assigned this fundamental as 1494 cm.$^{-1}$, *i.e.*, degenerate with number 19*a*, but the present choice is better established.[6]

Also in the b_1 class is the in-plane C–H deformation β(CH), number 3, with a calculated value of 1295 cm.$^{-1}$ in deuterobenzene.[13] Again, in fluorobenzene the assignment is satisfactory, but in phenol the value seems to be somewhat higher and the weak absorption in solution at 1313 cm.$^{-1}$ is assigned to the fundamental. This band is just detectable as a shoulder at about 1310 cm.$^{-1}$ in the spectrum of the vapour. In toluene, Kovner and Peregudov gave 1278 cm.$^{-1}$ for this fundamental, but Wilmshurst and Bernstein[9] took the value 1105 cm.$^{-1}$ which seems much too low. Possible values available from the spectrum obtained by the latter workers are 1260 or 1311 cm.$^{-1}$ the latter of which is chosen here, and the weak absorption at 1105 cm.$^{-1}$ is taken as $695 + 407 = 1102$ (B_1), in agreement with the observed type B contour. (Mecke and Greinacher[3b] similarly assigned the weak band in phenol at 1106 cm.$^{-1}$ as a b_1 fundamental but this is interpreted here as the same combination as in toluene.) Changes have also been made in two of the γ(CH) frequencies as given by Wilmshurst and Bernstein, their values 984 and 966 cm.$^{-1}$ in the a_2 and b_2 classes respectively being reassigned as 966 and 981 cm.$^{-1}$. These are in agreement with the more recent studies.[11,12]

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[8] Whiffen, *Spectrochim. Acta*, 1955, **7**, 253.

[9] Wilmshurst and Bernstein, *Canad. J. Chem.*, 1957, **35**, 911.

[10] American Petroleum Institute, Research Project 44, Catalogue of Infrared Spectra, nos. 308, 1685, 1704, 1714, 1716, 1783.

[11] Kovner and Peregudov, *Optika i Spectroskopiya*, 1958, **5**, 134.

[12] Fuson, Garrigou-Lagrange, and Josien, *Spectrochim. Acta*, 1960, **16**, 106.

[13] Brodersen and Langseth, *Kgl. danske Videnskab. Selskab, Mat.-fys. Skrifter*, 1959, **1**, 3.

The assignments for aniline have been made on the basis of C_{2v} symmetry to facilitate the comparison and use has been made of the Raman shifts[1] apart from four frequencies (3058, 1311, 1054, 964 cm.$^{-1}$) taken from the infrared spectrum.[14] Essentially the same assignment has been recently made by Evans,[15] who attributes the Raman line at 1340 to a combination, assigning number 14 as an infrared band at 1330 cm.$^{-1}$ in the liquid. Again, therefore, the correlation with the other assignments in Table 2 is quite satisfactory.

THERMODYNAMIC FUNCTIONS

The values of the fundamental frequencies for phenol listed in Table 2 were used to calculate the vibrational contributions to the thermodynamic functions by using the tables of Johnston, Savedoff, and Belzer.[16] To compute the rotational contributions the following dimensions were used: C–C, 1·397 Å; C–H, 1·084 Å; C–O, 1·428 Å; C–O–H angle 107°; all other angles 120°. For this model the product of the three principal moments of inertia was found to be $2{\cdot}34 \times 10^{-113}$ g.^{3} cm.^{6}, and the reduced moment of inertia for internal rotation was found to be $1{\cdot}46 \times 10^{-40}$ g. cm.^{2}. The symmetry numbers are 1 for overall rotation and 2 for internal rotation. The barrier height to free rotation of the OH group was taken as 3140 ± 285 cal. as determined by Kojima,[5] and the contributions of restricted rotation to the thermodynamic functions were obtained from the tables of Pitzer and Gwinn.[17] Units, values of the fundamental constants, and atomic weights were those of the American Petroleum Institute Research Project 44.[18]

From the calculated values of the thermodynamic functions for phenol as listed in Table 3, together with those[16] for C (graphite), H_2 (g), and O_2 (g), and the experimental heat of formation of gaseous phenol,[1] the values of ΔH_f°, ΔG_f°, and $\log_{10} K_f$ were calculated for the reaction:

$$6\text{C (graphite)} + 3\text{H}_2\text{ (g)} + \tfrac{1}{2}\text{O}_2\text{ (g)} = \text{C}_6\text{H}_5{\cdot}\text{OH (g)}$$

The entropy of phenol was measured by Parks, Huffman, and Barmore[19] and, in

TABLE 3. *The molal thermodynamic properties of phenol in the ideal-gas state.*

T (°K)	$-(G^\circ - H_0^\circ)/T$ (cal./deg.)	$(H^\circ - H_0^\circ)/T$ (cal./deg.)	$(H^\circ - H_0^\circ)$ (kcal.)	S° (cal./deg.)	C_p° (cal./deg.)	$-\Delta H_f^\circ$ (kcal.)[a]	ΔG_f°[a] (kcal.)	$\log_{10} K_f$[a]
0	0	0	0	0	0	18·63	−18·63	∞
273·16	60·17	13·18	3·60	73·35	22·70	22·72	−9·12	+7·30
298·16	61·36	14·07	4·19	75·43	24·75	23·05	−7·88	+5·78
300	61·45	14·13	4·24	75·58	24·90	23·07	−7·79	+5·68
400	66·01	17·79	7·12	83·80	32·45	24·12	−2·51	+1·37
500	70·37	21·37	10·68	91·74	38·64	24·92	+2·97	−1·30
600	74·56	24·67	14·80	99·23	43·54	25·55	+8·61	−3·14
700	78·59	27·65	19·36	106·24	47·44	26·06	+14·34	−4·48
800	82·46	30·33	24·26	112·79	50·62	26·40	+20·13	−5·50
900	86·18	32·73	29·46	118·91	53·26	26·65	+25·96	−6·30
1000	89·74	34·90	34·90	124·65	55·49	26·82	+31·82	−6·95

[a] Standard heat, standard free energy, and common logarithm of the equilibrium constant for the formation of phenol by the reaction: $6\text{C (graphite)} + 3\text{H}_2\text{ (g)} + \tfrac{1}{2}\text{O}_2\text{ (g)} = \text{C}_6\text{H}_5{\cdot}\text{OH (g)}$.

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[14] Mecke, D.M.S. Catalogue of Infrared Spectra, Butterworths, London, Nos. 2417, 3345, 3346.

[15] Evans, *Spectrochim. Acta*, 1960, **16**, 428.

[16] Johnston, Savedoff, and Belzer, " Contributions to the Thermodynamic Functions by a Planck–Einstein Oscillator in One Degree of Freedom," Office of Naval Research, Department of the Navy, Washington, D.C., 1949.

[17] Pitzer and Gwinn, *J. Chem. Phys.*, 1942, **10**, 428.

[18] Rossini, Pitzer, Arnett, Braun, and Pimental, " Selected Values of Physical Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Research Project 44, Pittsburgh, 1953.

[19] Parks, Huffman, and Barmore, *J. Amer. Chem. Soc.*, 1933, **55**, 2733.

conjunction with the measured heat of sublimation[1] and vapour-pressure data,[1] yields as follows an observed value for the entropy of phenol at 298·16° K:

S (crystals), 0—90° K	11·72	34·08 ± 0·50 [19]
S (crystals), 90—298° K	22·36	
$S_{\text{sublimation}}$ (16,410 + 120)/298·16		55·04 ± 0·4 [1]
$\boldsymbol{R} \ln p = \boldsymbol{R} \ln (0{\cdot}3431/760)$		−15·31 [1]
Estimated correction for gas imperfection		−0·001 [1]
$S°$ (observed), 298·16° K		73·81 ± 0·64 cal./deg.mole

This is to be compared with a calculated value of $S_{\text{trans.}} + S_{\text{rot.}} + S_{\text{vib.}} + S_{\text{int.rot.}} = 39{\cdot}54 + 26{\cdot}95 + 7{\cdot}19 + 1{\cdot}77 = 75{\cdot}44 \pm 0{\cdot}20$ cal./deg.mole. The difference between the two values is probably to be attributed to error in the large contribution to the entropy from 0—90° K, which was obtained by an extrapolation method. Moreover, with the assignment given above the observed entropy requires an internal rotation contribution of 1·63 cal./deg.mole, which is equivalent to a barrier height to free rotation greater than 12,000 cal., a value which is almost certainly far too high.

Experimental.—Infrared spectra of phenol, purified in this laboratory,[1] were recorded in carbon tetrachloride and carbon disulphide solutions by using the instrument described previously.[20] The region 16—21 μ was measured on a Grubb-Parsons GS2A spectrometer by Dr. A. E. Parsons, Basic Physics Division, N.P.L.

Raman shifts to 1600 cm.$^{-1}$ of the molten samples were measured in a Hilger photoelectric Raman spectrograph with Hilger source equipment.

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[20] Hales, *J. Sci. Inst.*, 1959, **36**, 264.