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The Vibrational Spectrum of Pyridine and the Thermodynamic Properties of Pyridine Vapors

CHARLES H. KLINE, JR.,* AND JOHN TURKEVICH

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

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An analysis of the vibrations of the pyridine molecule was made on the basis of infra-red, Raman, and ultraviolet absorption spectra. The fundamental frequencies were assigned and the thermodynamic properties of pyridine were calculated on the basis of such an assignment.

IN connection with catalytic studies on the synthesis of pyridine the thermodynamic properties of pyridine vapors at elevated temperatures were desired. As no experimental data are available, the required functions were calculated by statistical methods. Application of these methods required the determination of the fundamental frequencies in the vibrational spectrum of pyridine.

The observed vibrational spectrum of pyridine has frequently been recorded. The data available on pyridine and the recent thorough investigations on the closely related benzene spectrum¹⁻⁴ make possible a reasonably satisfactory analysis of the pyridine spectrum which is sufficiently accurate for the required statistical calculations.

Of the numerous investigations of the Raman spectrum of pyridine⁵⁻¹⁷ those of Venkateswaran,^{5, 9, 13} Krishnamurti,¹¹ Kohlrausch,^{14, 15, 18} and

Ananthakrishnan¹⁶ are the most accurate and extensive. The results of these investigators are given in the first four columns of Table I, which summarizes the observed lines in the pyridine spectrum and their assignments. Only three lines have been reported which were not found by these four investigators; these lines have no significance and appear to have been caused by impurities in the samples or to errors. The three lines are given in column five of Table I.

Henri and Angenot¹⁹ have analyzed the vibrational fine structure of the ultraviolet absorption spectrum of pyridine. The vibrational frequencies found by them are given in column six of Table I.

The infra-red absorption spectrum of liquid pyridine has been investigated three times in the region beyond 3μ , which contains all the fundamentals.²⁰⁻²² The infra-red absorption spectrum of pyridine vapor has recently been measured by Turkevich and Stevenson.²³ As the pyridine used by the earlier investigators appears to have been contaminated with α -picoline, the sample used by Turkevich and Stevenson was taken from a narrow-cut commercial pyridine and purified by three crystallizations of the pyridine—zinc-chloride double salt from absolute alcohol. This pyridine should therefore have been free of homologs and other impurities.²⁴ The results of the infra-red investigations appear in columns seven to ten of Table I.

* Now Ensign, USNR.

¹ Lord and Andrews, *J. Phys. Chem.* **41**, 149-158 (1937).

² Angus, Bailey, Ingold, Wilson, *et al.*, *J. Chem. Soc.*, pp. 912-987 (1936).

³ Langseth and Lord, *Kgl. Danske Vid. Sels. Math.-Fys. Medd.* **16**, No. 6, 85 pp. (1938).

⁴ K. S. Pitzer and Scott, *J. Am. Chem. Soc.* **65**, 803-829 (1943).

⁵ Ganesan and Venkateswaran, *Ind. J. Phys.* **4**, 195-280 (1929).

⁶ Okubo and Hamada, *Sci. Rep. Tôhoku Imp. Univ.* [I], **18**, 601-608 (1929).

⁷ Petrikaln and Hochberg, *Zeits. f. physik. Chemie* **B3**, 217-228, 405 (1929).

⁸ Bonino and Brüll, *Gazz. Chim. Ital.* **59**, 675-680 (1929).

⁹ Venkateswaran, *J. Phys. Chem.* **34**, 145-152 (1930).

¹⁰ C. E. Cleeton and R. T. Dufford, *Phys. Rev.* **37**, 362-372 (1931).

¹¹ Krishnamurti, *Ind. J. Phys.* **6**, 367-387 (1931).

¹² Whiting and Martin, *Trans. Roy. Soc. Canada* [III], **25**, Sec. 3, 87-98 (1931).

¹³ Venkateswaran, *Phil. Mag.* **15**, 263 (1933).

¹⁴ Kohlrausch and Pongratz, *Ber.* **B67**, 1474 (1934).

¹⁵ Kohlrausch, *Zeits. f. physik. Chemie* **B30**, 315 (1935).

¹⁶ Ananthakrishnan, *Proc. Ind. Acad. Sci.* **A3**, 52-74 (1936).

¹⁷ Bernstein and Martin, *Trans. Roy. Soc. Canada* [III], **31**, 95-103 (1937).

¹⁸ Herz, Kahovec, and Kohlrausch, *Zeits. f. physik. Chemie* **B53**, 124-148 (1943).

¹⁹ Henri and Angenot, *Comptes rendus* **201**, 895-896 (1935); *J. chim. phys.* **33**, 641-665 (1936).

²⁰ Coblentz, *Investigations of Infra-Red Spectra* (Washington, D. C., Carnegie Institute, 1905), Part I, pp. 96, 145, 272, 274, and insets.

²¹ Spence, *Astrophys. J.* **39**, 243-263 (1914).

²² Lecomte, *Comptes rendus* **207**, 395-398 (1938).

²³ J. Turkevich and P. C. Stevenson, *J. Chem. Phys.* **11**, 328-9 (1943).

²⁴ Heap, Jones, and Speakman, *J. Am. Chem. Soc.* **43**, 1936-1940 (1921); Mahan and Bailey, *ibid.* **59**, 2449-2450 (1937).

Column eleven gives averages for the observed lines. Columns twelve, thirteen, and fourteen give the depolarization factors for certain of the Raman lines as determined by Venkateswaran,¹³ A. W. Reitz (reported in reference 18), and Kohlrausch,¹⁸ respectively.

ANALYSIS OF THE SPECTRUM

The similarity of the spectra of benzene and pyridine has been remarked by a number of authors.^{5, 9, 10, 13, 15, 18, 19, 22} Depolarizations of the principal corresponding Raman lines are practically identical.¹³ The chemical similarity between benzene and pyridine is well known, and electron-diffraction data²⁵ show that the structures of the two molecules differ only negligibly.

The following discussion will show that the ring vibrations of pyridine parallel those of benzene and can be readily located; the hydrogen vibrations of pyridine show considerable divergence from those of benzene and can only be tentatively assigned.

Normal Modes of Vibration of Pyridine

The symmetry of pyridine is C_{2v} . This is the symmetry that results by replacing one $-CH$ group in benzene by a nitrogen atom; it is the symmetry of monodeuterobenzene³ and of pyrrole.²⁶ No higher symmetry is compatible with the established chemical structure of the molecule. Lower symmetries are improbable: A C_1 symmetry can at once be excluded, for it would require that all the Raman lines be polarized; a symmetry C_s , requiring that the molecule have only one vertical plane of symmetry, can be ruled out, as this would require that the molecule be aplanar or that it be planar but unsymmetrical, as if it were frozen into one of the two Kekulé resonance forms, for example.

Given a symmetry C_{2v} , we readily find the distribution of the twenty-seven fundamental frequencies into the four symmetry classes either by group theory²⁷ or the equivalent symmetry

theory.²⁸ Table II gives the various classes and the selection rules. In deriving Table II the two-fold rotational axis of symmetry through the nitrogen atom and the gamma-carbon atom is taken as the z axis. The x axis lies in the plane of the molecule; it is perpendicular to the z axis, which it intersects at the center of gravity of the molecule. The y axis is perpendicular to the plane of the molecule and intersects the x and z axes at the center of gravity.

As pyridine differs but little from benzene and as the observed pyridine spectrum is very similar to that of benzene, the normal modes of vibration of the two molecules must also be very similar. The normal modes of vibration of benzene have been calculated by the methods of group theory by Wilson;²⁹ they are shown schematically in Fig. 1, as given by Langseth and Lord.³ The low symmetry of pyridine makes such a calculation prohibitively laborious. The normal modes of pyridine, however, may as a first approximation be taken as those of benzene, except that three hydrogen vibrations (one stretching and two bending) will be lacking in pyridine.

Table III shows the changes in the symmetry classes on transition from a D_{6h} structure in benzene to a C_{2v} structure as in monodeuterobenzene and further to the C_{2v} structure of pyridine. Note that in Table III the translational and rotational motions are referred to different axes in the D_{6h} and C_{2v} structures.

On passing from a monosubstituted benzene (such as monodeuterobenzene) to pyridine a hydrogen stretching frequency disappears from class A_1 , a planar hydrogen bending frequency from class B_1 , and an out-of-plane hydrogen bending frequency from class B_2 . As the schematic vibration diagrams of Fig. 1 have no more than a qualitative significance for pyridine, it is highly arbitrary to speak of omitting any three specific vibrations; for convenience, however, the pyridine vibrations have been numbered according to the more or less analogous benzene vibrations, and vibrations $7a$, $9b$, and $17b$ have been omitted. It must be realized that this is only a matter of expediency.

²⁵ Schomaker and Pauling, J. Am. Chem. Soc. **61**, 1769 (1939).

²⁶ R. C. Lord, Jr., and F. A. Miller, J. Chem. Phys. **10**, 328-341 (1942).

²⁷ Rosenthal and Murphy, Rev. Mod. Phys. **8**, 317 (1936).

²⁸ Kohlrausch, *Der Smekal-Raman Effekt. Ergänzungsband* (Julius Springer, Berlin, 1938), p. 44.

²⁹ E. B. Wilson, Jr., Phys. Rev. **45**, 706 (1934).

TABLE I. The vibrational spectrum of pyridine.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	Raman spectrum (liquid)				UV (vap.)	Infra-red (liquid)			IR (vap.)	Av.	Depolarization			Assignment
Venkat.	Krish.	Kohl.	Ananth.	Others	H & A	Coblentz	Spence	Lecomte	T & S		Venk.	Reitz	Kohl.	(Fundamentals are underlined and starred)
				216 (2) ^a						216				Picoline
	371 (0)	374 (00)	377 (0)							374				*16b
405 (1)	403.6 (1)	405 (1)	402 (1)							404			0.72	*16a
				472 (3) ^b						472				Error
	553 (0)?		553 (0)							553				Picoline
603 (1)	603 (1½)	605 (3)	602 (1)		600			601 s	610 m	604	0.7	dp	0.73	**6a, 6b
									630 m	630				1028-404=624; 1037-404=633
651 (2)	651.9 (3)	652 (5)	652 (3)						650 m	652	0.8	dp	0.76	*4
									{ 662 669 s 690 }	669				*11
	717 (0)	710 (0)				709 (10)		708 s	710 m	710				*10b
	747 (0)	749 (0)				751 (7)		746 s	744 w	747				*10a
									763 w	763				374+404=778
	806 (0)	812 (0)	799 (0)					811 w	795 w	795				2×404=808
						806 (1)				807				Picoline; 2×404??
						840 (½)			833 w	836				1210-374=836?? 1440-604=836??
						855 (½)			847 w	850				1570-710=860??
884 (1)	885 (1)	886 (1)	878 (½)		857	886 (1)		890 w	881 w	884		(0.50)	(0.42)	*18a
						922 (½)			907 w	915				1570-652=918?
935 (0)	942 (0)	942 (0)?	942 (0)			949 (½)			936 m	941				*5
		980 (2)	979 (0)							980				1580-604=976 See text.
988 (10)	992 (10)	990 (10)	990 (10)		993	992 (5½)	985 s	984 s		990	0.1	0.04	0.05	*1
1027 (10)	1029.4 (10)	1029 (10)	1028 (10)		1031	1028 (4½)	1023 s	1020 s		1028	0.2	0.04	0.05	*12
		1043 (0)	1040 (0)			Shoulder			1037 s	1037				*18b
		1054 (0)?								1054				Picoline
	1067 (1)	1069 (1)	1057 (0)			1069 (3½)	1053 m	1052 w		1061				*17a
1157 (1)	1145 (1)	1144 (0)	1143 (½)		1159	1138 (3)	1137 m	1125 w	1136 w	1139		0.67	0.76	**9a, 15
									1156 w	1156				404+747=1151?
1217 (2)	1218 (3)	1218 (5)	1218 (3)			1211 (2½)	1202 m	1190 w	1202 w	1210	0.6	0.75	0.72	*3
				1268 (1) ^b					1263 w	1265				Picoline; 604+652=1256; 604+669=1273
						1290 (½)				1290				2×652=1304

TABLE I.—Continued.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	Raman spectrum (liquid)				UV (vap.)		Infra-red (liquid)		IR (vap.)	Av.	Depolarization			Assignment
Venkat.	Krish.	Kohlr.	Ananth.	Others	H & A	Coblentz	Spence	Lecomte	T & S		Venk.	Reitz	Kohl.	(Fundamentals are underlined and starred)
1376 (1)						1369 (1)			1376 w	1374				990 + 374 = 1364; Picoline?
	1439 (0)	1438 (1)	1444 (0)			1439 (6)	1438 s		1445 s	1440				*19b
1486 (0)	1483 (1½)	1480 (3)	1485 (1)			1481 (5)			{1481 } 1510 s	1485		p?	p	*19a
1576 (3)	{1571.4 (4) 1580.8 (2) 1596.7 (1)	1570 (5) 1580 (5) 1596 (2)	1570 (2) 1579 (2) 1594 (1)				1574 s { 1600 (5½) 1723 (1)			1570 1580 1598	0.8	dp	0.71	{*8b *8a 990 + 604 = 1594 See text.
						1923 (1B)	1915 w		1605 s	1598				*14
									1830 m	1830				884 + 941 = 1825 See text.
									1991 m	1920				990 + 941 = 1931
	2368 (½)	2368 (0) ?	2370 (0)							1991				941 + 1061 = 2002 See text.
	2455 (½)	2451 (0)	2449 (0)							2369				1485 + 884 = 2369 ??
	2651 (0)	2651 (0) ?	2658 (0)							2452				1440 + 1028 = 2468 ??
	2867 (½)	2868 (1)	2871 (0)							2653				1440 + 1210 = 2650 ??
	2913 (½)	2911 (1)	2908 (0)							2869				2 × 1440 = 2880 ??
	2952.2 (1)	2952 (1)	2951 (1)							2911				Picoline; 1440 + 1485 = 2925 ??
	2985 (½)	2988 (1)	2986 (0)							2952				2 × 1485 = 2970 ??
	3024 (1)	3023 (1)	3025 (½)							2986				
3033		3031 (0)	3034 (½)							3024				1440 + 1570 = 3010 ?
3056 (8)	3054 (10) ^c	3054 (5B)	3054 (8B)							3033	0.8			1440 + 1580 = 3020 ?
		3069 (0)	3063 (½)							3054	0.4		0.36	***2, 13, 7b (1485 + 1570 = 3055)
	3089 (½)	3090 (0)	3090 (½)			3076 (3½B)	3076 m			3066				1485 + 1580 = 3065 ?
	3144.1 (1½)	3143 (1)	3142 (1½)						3070 s	3075				**20a, 20b
	3175 (½)	3175 (1)	3172 (½)							3143				2 × 1570 = 3140 ?
										3174				2 × 1580 = 3160 ?

Notes: All frequencies are given in cm⁻¹. Kohlrausch's intensities and those of column 5 have been adjusted to the basis of an intensity 10 for the 990-cm⁻¹ line.

Symbols and abbreviations:

a, Bonino and Brüll, reference 8, observers.

b, Bernstein and Martin, reference 17, observers.

c, Line reported as having "rotational wings."

B, Broad line.

?, Question mark indicates uncertainty on the part of the authors whose results or proposals are recorded in the column where datum is questioned. In column 15, ? and ?? indicate uncertain and very uncertain assignment by the authors of the present paper.

s, Strong line.

m, Medium line.

w, Weak line.

p, Polarized line.

dp, Depolarized line.

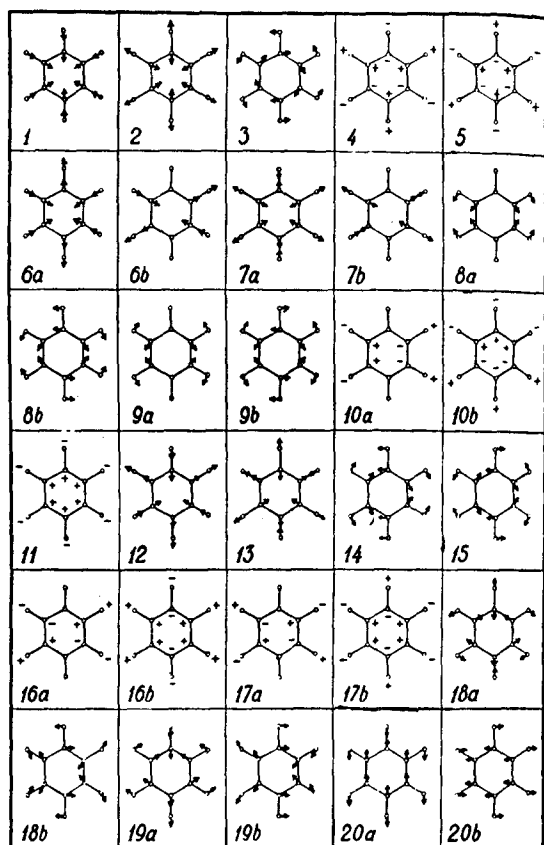


FIG. 1. Normal modes of vibration of benzene (Langseth and Lord, after Wilson). The two components of each degenerate vibration are denoted by *a* and *b*. Component *a* is symmetrical to a twofold axis through the para carbon atoms, and component *b* asymmetrical.

Ring Vibrations

Transition from a D_{6h} to a C_{2v} structure in benzene and related compounds releases the degeneracy of the ten degenerate benzene vibrations, and each degenerate frequency is split into two components, one symmetrical and one asymmetrical to the C_2^z axis. In monodeutero benzene the degenerate vibrations of the carbon ring of benzene appear as doublets with a separation of 3.5 to 55 cm^{-1} . In Table IV the ring vibrations of benzene are given as well as the corresponding vibrations of monodeutero benzene and the ring vibrations of pyridine as proposed in the present paper.

The great similarity of the three ring-vibration spectra of Table IV is very convincing evidence for the frequencies assigned to the ring vibrations of pyridine. The following detailed consideration

of the individual lines lends considerable support to the assignment.

ν_{16a} and ν_{16b} at 374 and 404 cm^{-1} are both weak in the Raman spectrum of pyridine, as in the deuterated benzenes.

ν_{6a} and ν_{6b} are both assigned to 604 cm^{-1} . These frequencies are similarly unresolved in the spectra of several of the deuterobenzenes. The occurrence of the 604- cm^{-1} line in the ultraviolet

TABLE II. Selection rules for pyridine (symmetry C_{2v}).

Class	Essential symmetry elements			Selection rules		Vibrations			
	C_2^z	σ_x	σ_y	Raman	I.R.	Trans. & Rot.	Ring	Hyd.	Total
A_1	<i>s</i>	<i>s</i>	<i>s</i>	<i>p</i>	<i>a</i>	T_z	5	5	10
A_2	<i>s</i>	<i>as</i>	<i>as</i>	<i>dp</i>	<i>ia</i>	R_z	1	2	3
B_1	<i>as</i>	<i>as</i>	<i>s</i>	<i>dp</i>	<i>a</i>	T_x, R_y	4	5	9
B_2	<i>as</i>	<i>s</i>	<i>as</i>	<i>dp</i>	<i>a</i>	T_y, R_x	2	3	5

TABLE III. Symmetry classes for benzene, monosubstituted benzenes, and pyridine.

Benzene	Monosubstituted benzene	Pyridine
A_{1g} { 1 (-, -) } B_{1u} { 12 (-, -) } E_{g+} { 6 (R, -) } E_{u-} { 18 (-, IR) } B_{2u} { 14 (-, -) } A_{2g} { 3 (-, -) } B_{2g} { 4 (-, -) } A_{2u} { 11 (-, IR) } E_{u+} { 16 (-, -) } E_{g-} { 10 (R, -) }	A_1 (R, IR) B_1 (R, IR) B_2 (R, IR) A_2 (R, -)	A_1 (R, IR) B_1 (R, IR) B_2 (R, IR) A_2 (R, -)

vibrational spectrum shows that there must be a totally symmetric vibration of this frequency. The high depolarization factor of the Raman line may result from the coincidence of the non-totally symmetric vibration ν_{6b} .

The exact location of ν_4 in benzene is in some doubt: Langseth and Lord estimate it to be at 664 cm^{-1} by the product rule, and Pitzer and Scott have assigned it to the weak Raman line appearing in violation of the selection rules at 685 cm^{-1} in liquid benzene. In pyridine ν_4 is probably the rather strong Raman line at 652 cm^{-1} . This frequency appears too intense to be correlated with the powerful infra-red line at 669 cm^{-1} . Furthermore, this infra-red line has a pronounced shoulder at about 650 cm^{-1} , which argues for the existence of an independent line at this point. ν_4 is allowed in both infra-red and Raman spectra in pyridine.

ν_1 and ν_{12} , the powerfully polarized Raman lines at 990 and 1028 cm^{-1} , both fall in the same symmetry class in pyridine and by the customary interaction are displaced away from each other appreciably more than in benzene. The separation between ν_1 and ν_{12} is 18 cm^{-1} in benzene, 28 cm^{-1} in monodeuterobenzene, and 38 cm^{-1} in pyridine. The complete absence of ν_1 from the infra-red spectrum of pyridine vapor is interesting in view of the intensity of this line in the infra-red spectrum of the liquid. ν_1 is forbidden by symmetry in the infra-red spectrum of benzene vapor but may be the line appearing in the liquid at about 985 cm^{-1} as a shoulder on the strong line at 1033 cm^{-1} . The absence of ν_1 from the infra-red spectrum of pyridine vapor illustrates very strikingly the manner in which pyridine behaves almost as if it had the D_{6h} symmetry of benzene.

ν_{19b} and ν_{19a} are assigned to 1440 and 1485 cm^{-1} , respectively, in pyridine. The line at 1485 cm^{-1} appears as a doublet in the infra-red spectrum of pyridine vapor, the two components being located at 1481 and 1510 cm^{-1} . This doublet probably represents the imperfectly resolved P and R branches; the observed separation of 29 cm^{-1} is not far from the separation of 23 cm^{-1} found between the P and R branches of the 1485-cm^{-1} line of benzene in the more accurate measurements of Bailey, Hale, Ingold, and Thompson.² Assignment of the totally symmetric

TABLE IV. Ring vibrations of benzene, monodeuterobenzene, and pyridine.

Vibration	Benzene		Monodeutero- benzene	Pyridine
	L&L	P&S	L&L	
$16b$	406		381	374
$16a$			403	404
$6a$	606.4		598.5	$604\}^a$
$6b$			602.0	$604\}^a$
4	664^b	685^c	—	652
1	992.5		980.9	990
12	1010^b		1008.6	1028
$19b$	1485		1418 ??	1440
$19a$			1473 ^b	1485
$8b$	1595		1575.7	1570
$8a$			1593.8	1580
14	d	1693^c	—	1723

Notes: Frequencies in cm^{-1} .

L&L, Langseth and Lord, reference 3.

P&S, Pitzer and Scott, reference 4.

^a, component of an unresolved doublet.

^b, calculated from Teller's product rule.

^c, appears in the Raman spectrum of liquid benzene although

forbidden by the selection rules.

^d, Lord and Andrews (reference 1) calculate 1854 cm^{-1} .

??, assignment considered doubtful by Langseth and Lord.

ν_{19a} to 1485 cm^{-1} rather than to 1440 cm^{-1} is supported by the depolarization data and the greater intensity of the 1485 cm^{-1} Raman line.

Release of the degeneracy of ν_8 in benzene (at 1595 cm^{-1}) on transition to pyridine gives a difficultly resolvable doublet at 1570 and 1580 cm^{-1} . In benzene there is also another rather strong line at 1604 cm^{-1} representing the combination $\nu_1 + \nu_6$, which is much stronger in the Raman spectra than is customary for combination tones because of resonance with ν_8 . A similar situation occurs in pyridine, where besides the ν_{8a} , ν_{8b} doublet there occurs a strong Raman line at 1598 cm^{-1} representing $\nu_1 + \nu_6$. Resonance between $\nu_1 + \nu_6$ and ν_8 has the further effect of causing a satellite to ν_1 to appear in the pyridine spectrum at 980 cm^{-1} similar to the satellites at 979.6 and 999.0 cm^{-1} in benzene. Because of the resonance between ν_8 and $\nu_1 + \nu_6$ and the consequent mixing of the wave functions a vibrational transition from the first excited level of ν_6 to either the ν_{8b} (1580 cm^{-1}) or $\nu_1 + \nu_6$ (1598 cm^{-1}) lines gives rise to Raman scattering differing but little (except in intensity) from the scattering caused by transition of ν_1 from the ground state

to the first excited state. Two satellites to the 990-cm^{-1} line (ν_1) should therefore be found at $1580 - 604 = 976\text{ cm}^{-1}$ and $1598 - 604 = 994\text{ cm}^{-1}$. The faint Raman line at 980 cm^{-1} in pyridine may be taken as the first difference; the second satellite is extremely weak in benzene and has doubtless not been observed in pyridine because of the nearness to 990 and 1028 cm^{-1} . The two remaining satellites to ν_1 in benzene (at 984 and 1005 cm^{-1}) arise from isotopic impurity, about 6 carbon atoms in every 100 being C^{13} . In pyridine C^{13} substitution can occur in three non-equivalent positions in the ring, and isotopic satellites to the different lines are doubtless too weak ever to be observed.

ν_{14} has never been definitely located in benzene, where the vibration is forbidden in both Raman and infra-red spectra. Lord and Andrews¹ calculated from Wilson's force constants the value $\nu_{14} = 1854\text{ cm}^{-1}$. Angus *et al.* calculated² $\nu_{14} = 1720\text{ cm}^{-1}$. From consideration of the other planar carbon bending frequencies Langseth and Lord³ estimated that ν_{14} lies in the region $1440\text{--}1900\text{ cm}^{-1}$. Pitzer and Scott⁴ have chosen the weak Raman line at 1693 cm^{-1} to represent this vibration, on the assumption that this line appearing in the spectrum of this liquid may represent a forbidden line because of the relaxation of the selection rules in the liquid state.

In pyridine there are four possibilities for ν_{14} , the two infra-red lines of the liquid at 1723 and 1920 cm^{-1} and the two infra-red lines of the vapor at 1830 and 1991 cm^{-1} . Because of the close similarity in the vapor-phase spectra of pyridine and benzene it seems unlikely that either of the vapor lines represents ν_{14} . Furthermore these two lines are very similar to the lines in benzene vapor at 1808 and 1961 cm^{-1} , which Pitzer and Scott explain as the allowed combinations $\nu_{10} + \nu_{17}$ and $\nu_5 + \nu_{17}$, respectively. The pyridine lines can also be assigned to these combinations on the basis of the assignment of fundamentals proposed here. Of the two lines in the liquid that at 1920 cm^{-1} lies somewhat too high for a ring vibration, and ν_{14} has therefore tentatively been assigned to 1723 cm^{-1} . In any event this cannot be far wrong.

The Hydrogen Vibrations

Although the ring vibrations of pyridine can be elucidated in a reasonably satisfactory manner,

the hydrogen vibrations can be located only in an approximate fashion. There appear to be differences in the force-constants of some of the pyridine vibrations as compared with the similar benzene vibrations. Thus, for example, attempts to locate the hydrogen frequencies of pyridine between the hydrogen frequencies of equivalent symmetry in benzene fail although a well-known theorem in dynamics states that if a system loses one degree of freedom then the $(s-1)$ new frequencies lie in the intervals between the s frequencies of the original system.

In general, transition from benzene to pyridine causes a displacement of the hydrogen frequencies toward lower frequencies; this is especially marked in some of the bending vibrations.

Class A_1

This class includes the totally symmetric vibrations; the frequencies are allowed in both Raman and infra-red spectra and appear in the ultra-violet vibrational spectrum. The ring frequencies are ν_1 , ν_{6a} , ν_{8a} , ν_{12} , and ν_{19a} .

Of the five hydrogen frequencies three belong to stretching vibrations and can be immediately assigned to the region $3050\text{--}55\text{ cm}^{-1}$. The totally symmetric stretching frequency ν_2 should be weak or missing in the infra-red; it is represented by the strong polarized Raman line at 3054 cm^{-1} . The antitranslational stretching ν_{20a} (as well as ν_{20b}) is assigned to the strong, rather broad infra-red line at 3075 cm^{-1} ; it seems likely that here as in monodeuterobenzene ν_{20a} and ν_{20b} form an unresolved doublet.

The position of ν_{13} is somewhat uncertain. The Raman line at 3054 cm^{-1} is surrounded by several satellites; these form a regular series corresponding to the combination tones $\nu_{19b} + \nu_{8b}$, $\nu_{19b} + \nu_{8a}$, $\nu_{19a} + \nu_{8b}$ (not observed but would be obscured by the strong line at 3054 cm^{-1}), and $\nu_{19a} + \nu_{8a}$, and it may be conjectured that these lines actually represent combination tones strengthened by resonance with ν_2 . As no valid assignments for ν_{13} and for ν_{7b} of class B_2 suggest themselves, both these frequencies are assigned with ν_2 to 3054 cm^{-1} . These lines cannot be far distant, and the assignment proposed even if in error makes only a negligible difference in the calculation of thermodynamic quantities.

There remain in this class two hydrogen bending frequencies, $\nu 9a$ and $\nu 18a$, which are assigned to 1139 and 884 cm^{-1} , respectively. These two lines appear in the ultraviolet vibrational spectrum of Henri and Angenot^{19*} and as they cannot be overtones must correspond to totally symmetric vibrations. Exact polarization data on the Raman line at 884 cm^{-1} are difficult, as the only intense observed line corresponding to this vibrational shift ($22,050 \text{ cm}^{-1} = \text{Hg } e-888$) falls very near the strong highly polarized line $\nu 1$ ($22,006 \text{ cm}^{-1} = \text{Hg } f-989$). The correctness of the location of $\nu 18a$ at 884 cm^{-1} therefore depends entirely on the correct analysis of the ultraviolet vibrational spectrum.

For $\nu 9a$ the ultraviolet line at 1159 cm^{-1} is correlated with the Raman and infra-red line at 1139 cm^{-1} , although this line appears but very slightly polarized if at all.

Class B₁

This class includes the vibrations in the plane of the molecule antisymmetric to the twofold rotational axis. The ring vibrations are $\nu 6b$, $\nu 8b$, $\nu 14$, and $\nu 19b$. The two hydrogen stretching frequencies $\nu 7b$ and $\nu 20b$ have already been assigned to 3054 cm^{-1} and 3075 cm^{-1} . There are three hydrogen bending frequencies corresponding to the four frequencies $\nu 3$, $\nu 9b$, $\nu 15$, and $\nu 18b$ in benzene; the assignment proposed is:

$$\nu 3 = 1210, \quad \nu 15 = 1139, \quad \nu 18b = 1037 \text{ cm}^{-1}.$$

$\nu 3$ and $\nu 15$ lie in the general range 1100–1300 cm^{-1} .

$\nu 18b$ is assigned to 1037 cm^{-1} where there is an intense infra-red line which appears to be different from $\nu 12$ at 1028 cm^{-1} . A weak Raman line is also found at this point. $\nu 12$ is forbidden in the infra-red in benzene, and it seems unlikely that it would be so intense in pyridine vapor as the observed line at 1037 cm^{-1} .

$\nu 15$ is assigned to 1139 cm^{-1} . Two lines appear to be present in this region, of which one probably represents $\nu 9a$ and the other either $\nu 15$ or a combination tone.

Class B₂

This class contains those vibrations out of the plane of the molecule and antisymmetric to the

* Henri and Angenot themselves correlate the UV line at 857 cm^{-1} with the Raman line at 884 cm^{-1} .

twofold rotational axis. The ring vibrations are $\nu 4$ and $\nu 16b$. Three hydrogen vibrations are formed from $\nu 5$, $\nu 10b$, $\nu 11$, and $\nu 17b$ in benzene. $\nu 11$, the out-of-plane antitranslational bending is readily assigned to the strong infra-red line at 669 cm^{-1} , whose *P*, *Q*, and *R* branches are very similar to those of the corresponding line in benzene. $\nu 5$ is assigned to 941 cm^{-1} , somewhat lower than its position in benzene. $\nu 10$ in benzene is very intense in the infra-red spectrum of the liquid; the doublet $\nu 10a$, $\nu 10b$ in pyridine is assigned to 747 and 710 cm^{-1} , respectively, as both of these lines are very strong in the infra-red absorption of the liquid. In the vapor the line at 710 cm^{-1} appears as a shoulder on the strong infra-red line at 669 cm^{-1} . A weak line is also found at 744 cm^{-1} ; this probably represents the overtone $2 \times \nu 16b = 748 \text{ cm}^{-1}$ as $\nu 10a$ is forbidden in the infra-red of pyridine.

Class A₂

This class contains the out-of-plane vibrations symmetrical to the twofold rotational axis. Frequencies are forbidden in the infra-red. The one ring vibration $\nu 16b$ falls at 374 cm^{-1} . Of the two hydrogen frequencies $\nu 10a$ has already been located at 747 cm^{-1} , and $\nu 17a$ is assigned to 1061 cm^{-1} , which is somewhat higher than the corresponding benzene frequency.

This assignment permits an explanation for the two infra-red lines at 1830 and 1991 cm^{-1} similar to that proposed by Pitzer and Scott for the corresponding benzene lines:

$$\begin{aligned} \nu 10a + \nu 17a &= 747 + 1061 = 1808 \text{ cm}^{-1}, \\ \nu 5 + \nu 17a &= 941 + 1061 = 2002 \text{ cm}^{-1}. \end{aligned}$$

Another assignment for 1808 cm^{-1} , however, seems more reasonable, as shown in Table I.

Other Lines Observed

Pyridine is notoriously difficult to purify, and commercial grades show a wide boiling range. The appearance of an unexplained group of lines in the pyridine spectrum suggests that the pyridine samples of the majority of investigators contained traces of α -picoline. The separation of this substance (b.p. 128°C) from pyridine (b.p. 115.5°C) requires distillation in a still of high

TABLE V. Principal lines of liquid α -picoline.

Infra-red (Ref. 20)	Raman (Ref. 18)
	207 (4)
	547 (5)
	628 (3)
755 (10)	801 (6)
	813 (4)
993 (6)	996 (8)
1044 (7)	1048 (9)
1144 (4)	1235 (3)
	1374 (3)
1458 (6)	1568 (3)
1595 (8)	1592 (3)
	2922 (3)
2976 (5)	3041 (3)
	3066 (3)

efficiency, or careful chemical purification as employed by Turkevich and Stevenson.²³

Table V gives the principal lines of α -picoline; it will be observed that in each case the lines are either present as weak unexplained lines in the pyridine spectrum or would be obscured by strong pyridine fundamentals. The suspected lines are missing in the vapor-phase infra-red spectrum of Turkevich and Stevenson.

The remaining lines of the pyridine spectrum are overtones and combinations, for which possible assignments are suggested in Table I.

THERMODYNAMIC PROPERTIES OF PYRIDINE

With the twenty-seven fundamental vibration frequencies of pyridine located in at least an approximate fashion, the thermal properties of pyridine vapors in the ideal-gas state may readily be calculated. Table VI summarizes the calculation of the entropy of the vapors at 25°C and one-atmosphere pressure; comparison with the experimentally measured value corrected to the ideal-gas state at one atmosphere shows good agreement. This shows that the frequencies proposed as fundamentals have at least an approximately correct distribution in the spectrum.

Table VII gives values of the free energy function $-(F^\circ - E_0^\circ)/T$, the heat content function $(H^\circ - E_0^\circ)$, and the heat capacity C_p° for pyridine vapors in the ideal-gas state at one-atmosphere pressure and temperatures up to 1000°K. These data are probably correct to

within about five percent and should be sufficient for most engineering and thermodynamic calculations. Actual pyridine vapors probably differ appreciably from an ideal gas, so an appropriate equation of state should be used in calculations. These data permit the determination of equilibria involving pyridine with fair accuracy and the limiting factor is now the considerable uncertainty in the heat of combustion of pyridine.

In determining the thermal functions of Tables VI and VII the structure of pyridine was determined from the electron diffraction data of Schomaker and Pauling.²⁵ These authors calculated an average ring-bond distance of 1.385 ± 0.01 A.U., from which, assuming a carbon-carbon bond length of 1.39 A.U. as in benzene, they found the carbon-nitrogen bond length in pyridine to be 1.37 ± 0.03 A.U.

To determine the bond angles it was assumed that the angles on each of the five carbon atoms were equal; these angles are then calculated to be 119.6° and the ring bond angle on the nitrogen

TABLE VI. Entropy of pyridine vapor in the ideal-gas state at one atmosphere and 25°C.

<i>By statistical calculation:</i>	
Translation and rotation	63.21 E. U./mole
Vibration	4.96
Total	68.17 E. U./mole
<i>By experimental data:</i>	
Entropy of liquid pyridine at 298.15°K	42.8 \pm 0.4 E. U./mole
Entropy of vaporization	33.0 \pm 0.3
Correction of actual gas at 20.7 mm* to ideal gas at 20.7 mm	0.0
Compression to 760 mm	-7.2
Total	68.6 \pm 0.7 E. U./mole

* Vapor pressure of pyridine at 25.0°C.

TABLE VII. Thermodynamic functions of pyridine vapor (for the ideal-gas state at one atmosphere).

T°K	$-(F^\circ - E_0^\circ)/T$ (Cal./degree)	$(H^\circ - E_0^\circ)$ Kcal./mole	C_p° Cal./degree
291.15	56.30	3.324	19.25
298.15	56.57	3.458	19.72
300	56.65	3.495	19.85
400	60.39	5.810	26.30
500	63.95	8.723	31.68
600	67.36	12.11	35.99
700	70.69	15.90	39.50
800	73.85	19.98	42.35
900	76.92	24.35	44.74
1000	79.87	28.93	46.76

atom 122.0° . It was further assumed that the carbon-hydrogen bonds bisect the angle supplementary to the ring bond angle. Using these assumptions the center of gravity of the molecule is found to lie on the C_2 axis 1.36 A.U. above the nitrogen atom. This gives $\log ABC = -113.226$.

The 1941 atomic weights were used, and the tables of Wilson, as given by Aston for the new physical constants, for the harmonic oscillator contributions to the thermal functions.³⁰

The experimental entropy of the vapor was based on the value of Parks, Todd, and Moore³¹

³⁰ Taylor and Glasstone, editors, *A Treatise on Physical Chemistry* (D. Van Nostrand Company, Inc., New York, 1942), Edition 3, Vol. I, Chap. IV.

³¹ Parks, Todd, and Moore, *J. Am. Chem. Soc.* **58**, 398 (1936).

for liquid pyridine. The vapor pressure and entropy of vaporization at 25°C were calculated from the vapor-pressure equation of van der Meulen and Mann.³² Expansion of the vapor to infinite volume by the Berthelot equation of state and recompression to the vapor pressure at 25°C by the ideal gas law gave a negligible correction of -0.006 E.U.

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³² van der Meulen and Mann, *J. Am. Chem. Soc.* **53**, 451-453 (1931).