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## Near Ultraviolet Absorption of Pyridine Vapor

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The absorption spectrum of pyridine at 3000–2500Å has been studied in the first order of a 3-m grating spectrograph. The band system represents an electronic transition  $A_1 \rightarrow B_1$  (using symmetry  $C_{2v}$  for pyridine). Several progressions of totally symmetric vibrations are observed. The band  $34769\text{ cm}^{-1}$  is taken as 0,0 band. Besides carbon ring vibrations the occurrence of hydrogen vibrations is established and discussed.

## INTRODUCTION

SINCE the investigation of the near ultraviolet absorption spectrum of pyridine vapor by Henri and Angenot,<sup>1</sup> much theoretical progress has been made in the interpretation of polyatomic spectra. As the analysis of the pyridine spectrum is important as basis for an interpretation of the spectra of pyridine derivatives and as the latter are of physical, chemical, and biological interest, it was felt that a reinvestigation of the pyridine spectrum was well justified. A preliminary report of this analysis has been published recently.<sup>2</sup>

## EXPERIMENTAL

As in previous work the spectrum was photographed in the first order (dispersion 5.54Å per mm) of a 3-m grating spectrograph (Eagle mounting) with a hydrogen discharge lamp of the ordinary type as light source. The pyridine was a commercial Merck product. It was purified<sup>3</sup> by distilling it twice under ordinary pressure and then a third time after letting it stand over potassium hydroxide for some time. The substance was finally carefully introduced into quartz absorption tubes of 15- and 75-cm lengths by vacuum distillation. During exposures the pyridine was kept in a side arm at temperatures varying from  $-60^\circ\text{C}$  to  $+32^\circ\text{C}$ , covering pressures from a few hundredths to 30 mm. An iron

arc furnished the comparison spectrum. Eastman spectroscopic plates I 0 and II 0 were used. Exposure times varied from 20 minutes to 3 hours. The measured wave-lengths of the bands agree well with those of Henri and Angenot. Wherever possible, the edges on the violet side were measured. The appearance of the bands will be discussed later.

Table I contains our measurements, visual intensity estimates and interpretations. We have observed much fewer bands than Henri and Angenot. This might be owing to the circumstance that their measurements cover a larger variety of pressure and temperature changes than ours; for example we have not repeated a study of the temperature dependence which brings out bands from higher vibrating levels in the ground state. A number of these bands, not measured by ourselves, are included, as they fit into our progressions.

The intensity estimates refer to particular experimental conditions which are stated in the column under "Intensity." Henri and Angenot used a more detailed classification of intensities based on a more precise study of the conditions under which the bands make their first distinct appearance. Although we have made use, for our interpretation, of their intensity data besides our own, we give in Table I only our own estimates.

Figure 1 represents the absorption spectrum of pyridine vapor.

## DISCUSSION AND ANALYSIS

The pyridine molecule belongs to symmetry group  $C_{2v}$  like many substituted benzenes. But

<sup>1</sup> V. Henri and P. Angenot, *J. de Chim. Phys.* **33**, 641 (1936). See their previous references.

<sup>2</sup> H. Sponer, *Rev. Mod. Phys.* **16**, 224 (1944).

<sup>3</sup> We wish to express our indebtedness to Dr. G. P. Handler of the Biochemistry Department of Duke Medical School and to Dr. M. B. Hall of the Physics Department (now with E. I. Dupont de Nemours and Company, Wilmington, Delaware) for the purification of the sample.

TABLE I. Absorption bands of pyridine.

Wave- number	Separation from 0—0 band	H-A	Intensity This research	Assignment	Wave- number	Separation from 0—0 band	H-A	Intensity This research	Assignment
*32 488	-2281	ew		0-1218-1063; 0-1218-2×601+(139); 0-2×1141.	777	-992	vw		0-992; 0-(395)-601.
* 503	-2266	ew		0-2×601-1063; 0-4×601+(139).	824	-945	w		0-945.
* 520	-2249	ew		0-1031-1218.	* 843	-926	vw		0+(139)-1063; 0-2×164-601.
* 557	-2212	ew		0-995-1218.	* 860	-909	w		
* 606	-2163	ew		0-945-1218.				<i>t</i> =31°C <i>p</i> =28.5 mm tube 15 cm	
* 677	-2092	ew		0-891-2×601; 0-1031-2×601+(139).	878	-891	w		0-891; 0+(139)-1031.
* 704	-2065	ew		0-2×1031.	901	-868	w		0-(395)-601+(139)?
* 799	-1970	ew		0-1372-601; 0-1031-945?	* 957	-812	ew		0-2×405?
* 935	-1834	ew		0-891-945; 0-1031+(139)-945.	34 003	-766	w		0-601-164.
* 951	-1818	ew		0-1218-601.	* 010	-759	vw		0-2×378?
* 970	-1799	ew		0-3×601.	057	-712	vw		0-712.
* 986	-1783	ew		0-2×891.	073	-696	vw		
*33 027	-1742	ew		0-601-1141.	091	-678	vw		0-1218+542.
* 101	-1668	ew		0-1063-601; 0+(139)-3×601.	111	-658	mw		0-2×601+542.
* 137	-1632	ew		0-1031-601.	120	-649	m	vw	0-649.
* 163	-1606	ew		0-945-601-59.	168	-601	sl	m	0-601; 0-1141+542.
* 225	-1544	ew		0-945-601.	191	-578	vw		0-1063-601+2×542; 0+(139)-3×601+2×542.
* 278	-1491	ew		0-891-601; 0-1491; 0-2×747?	* 201	-568	vw		0+(139)-712.
* 310	-1459	ew		0-(395)-1063; 0-712-747?	* 211	-558	vw		0-1141+581.
* 397	-1372	ew		0-1372? 0-995-374?	* 226	-543	vw		0-378-164? 0+(672)-1218?
			<i>t</i> =32°C <i>p</i> =31 mm tube 75 cm		250	-519	w	vw	0-1063+542; 0+(139)-2×601+542
* 410	-1359	ew		0-712-649? 0-2×945+542?	262	-507			
* 496	-1273	vw		0-1218-59.	282	-487	m	w	0-1031+542.
* 512	-1257	vw		0-2×601-59.	305	-464	mst	mw	0+(139)-601.
* 525	-1244	vw		0-2×891+542.	322	-447	w		0-992+542; 0-1031+581.
551	-1218	w		0-1218.	364	-405	ew		0-405; 0-945+542.
567	-1202	w		0-2×601; 0-1141-59.	374	-395	mw		0-(395); 0+(672)-1063?
* 587	-1182	vw		0-1031-151?	* 391	-378	vw		0-378.
* 628	-1141	vw		0-1141; 0-(395)-747?	408	-361	wd	vw	0+(672)-1031.
* 654	-1115	vw		0-1063-59; 0+(139)-3×601+542.	427	-345	mst	mw	0-891+542.
* 665	-1104	vw		0-(395)-712? 0-945-164?	446	-323	mw	w	0-1218+899; 0-2×164; 0+(672)-992.
* 681	-1088	w		0-1031-59.	462	-307	vw	ew	0-2×151?
* 692	-1077	vw		0+(139)-1218.	501	-268	wd	vw	0-2×405+542; 0+(672)-945?
706	-1063	w		0-1063; 0+(139)-2×601.	516	-253	wd	vw	0-1218+968.
738	-1031	mw		0-1031.	549	-220		vw	0-1218+995; 0-164-59; 0+(672)-891.
* 758	-1011	vw		0-945-59.	* 566	-203	w		0-1218+1017.
					592	-177		w	

TABLE I.—Continued.

Wave- number	Separation from 0—0 band	H-A	Intensity This research	Assignment	Wave- number	Separation from 0—0 band	H-A	Intensity This research	Assignment
			$t = -16^{\circ}\text{C}$ $p = 1 \text{ mm}$ tube 15 cm					$t = -19^{\circ}\text{C}$ $p = .9 \text{ mm}$ tube 15 cm	
605	-104		<i>w</i>	<i>mw</i> 0-405+241; 0-1031+864; 0-1063+899?	350	581		<i>vw</i>	0+581; 0-1218+2×899.
* 618	-151	<i>w</i>		0-378+226.	393	624		<i>w</i> <i>vw</i>	0+(139)+2×542-601; 0-(395)+1017?
* 636	-133	<i>vw</i>		0-1031+899; 0-1218+2×542.	407	638		<i>w</i> <i>vw</i>	0-992+3×542.
657	-112		<i>wd</i>	<i>wd</i> 0-649+542?; 0-2×59?	441	672		<i>mst</i> <i>m</i>	0+(672); 0-2×164+995.
* 693	-76	<i>vw</i>		0-945+864?; 0+(672)-747?	493	724		<i>wd</i>	
711	-58		<i>w</i>	<i>m</i> 0-601+542.	521	752		<i>wd</i>	
721	-48		<i>w</i>	<i>m</i> 0-945+899; 0-1063+1017.	544	775		<i>wd</i>	0-1218+2×995.
735	-34			<i>vw</i> 0-1031+995.	567	798		<i>wd</i>	0+864-59?
769	0		<i>mst</i>	<i>st</i> 0-0.	* 607	838	<i>wd</i>		0+(672)+542-378?; 0+995-161?
779	+10		<i>ew</i>	<i>vw</i> 0-891+899?	633	864		<i>mst</i> <i>m</i>	0+864.
* 793	+24	<i>w</i>		0-1063+2×542; 0+(672)-649.	668	899		<i>vw</i> <i>ew</i>	0+899.
812	43		<i>vw</i>	<i>w</i> 0-1141+1184?	677	908		<i>vw</i>	0+968-59; 0+(672)+241.
822	53		<i>vw</i>	<i>w</i> 0-1031+2×542; 0-945+995.	695	926	<i>w</i>		0+2×542-164.
831	62		<i>vw</i>	<i>w</i> 0-1031+968.	737	968		<i>mw</i> <i>w</i>	0+968.
841	72		<i>vw</i>	<i>w</i> 0-945+1017; 0+(672)-601.	764	995		<i>mst</i> <i>mst</i>	0+995.
849	80		<i>w</i>	<i>mw</i> 0+(139)-59; 0-891+968.	* 771	1002	<i>vw</i>		0+(139)+864.
874	105		<i>ew</i>	<i>vw</i> 0-891+995; 0+(139)+995-1031.	786	1017		<i>wd</i> <i>wd</i>	0+1017; 0-601+3×542?
908	139		<i>m</i>	<i>mst</i> 0+(139).	826	1057		<i>wd</i> <i>wd</i>	
922	153		<i>ew</i>	0-(395)+542.	855	1084		<i>st</i> <i>st</i>	0+2×542.
950	181		<i>vw</i>	<i>w</i> 0-(395)+581?; 0+(672)+542-1031.	* 872	1103	<i>vw</i>		0+(139)+968.
975	206		<i>w</i>	<i>mw</i>	* 889	1120	<i>vw</i>		0-601+2×864.
989	220		<i>ew</i>	<i>vw</i>	908	1139		<i>wd</i> <i>wd</i>	0+(139)+995.
* 993	224	<i>vw</i>		0+(672)+542-992; 0+226.	* 929	1160	<i>w</i>		0+2×581; 0+(139)+3×542-601.
35 032	263		<i>ew</i>	<i>w</i> 0-601+864; 0+(672)-405; 0+(672)+542-945?	944	1175		<i>w</i> <i>w</i>	0+1175?
047	278		<i>ew</i>	<i>wd</i> 0-2×405+2×542.	953	1184		<i>mw</i> <i>w</i>	0+1184?
075	306		<i>vw</i>	<i>wd</i> 0-712+1017?	984	1215		<i>mw</i> <i>w</i>	0+(672)+542.
100	331		<i>mw</i>	<i>mst</i>	989	1220		<i>mw</i> <i>w</i>	0+(139)+2×542.
117	348		<i>w</i>	<i>m</i> 0-649+995.	*36 030	1261	<i>vw</i>		
147	378		<i>w</i>	<i>mw</i> 0+542-164.	052	1283		<i>wd</i> <i>wd</i>	
165	396		<i>mw</i>	<i>mst</i> 0-601+995; 0+542-161?	073	1304		<i>wd</i> <i>wd</i>	
190	421		<i>mw</i>	<i>mst</i> 0-2×59+542.	091	1322		<i>wd</i> <i>wd</i>	0+(139)+1184.
* 202	433	<i>wd</i>		0-649+2×542.	137	1368		<i>wd</i> <i>wd</i>	0+995+542-164.
224	455		<i>ew</i>	<i>vw</i> 0+2×226.	160	1391		<i>m</i> <i>m</i>	0+2×995-601.
254	485		<i>mw</i>	<i>mst</i> 0-601+2×542; 0+2×241.	172	1403		<i>m</i> <i>mw</i>	0+542+864.
311	542		<i>st</i>	<i>st</i> 0+542	220	1451		<i>wd</i>	
					* 230	1461	<i>vw</i>		0+3×542-164.
					257	1488		<i>wd</i>	
					271	1502		<i>wd</i>	
					281	1512		<i>vw</i>	0+542+968.
					307	1538		<i>st</i>	0+542+995; 0+(672)+864.

TABLE I.—Continued.

Wave- number	Separation from 0—0 band	H-A	Intensity This research	Assignment	Wave- number	Separation from 0—0 band	H-A	Intensity This research	Assignment
341	1572		<i>w</i>	0+(672)+899.	933	2164		<i>wd</i>	0+4×542?
353	1584		<i>vw</i>		942	2173		<i>vwd</i>	0+4×542?
397	1628		<i>msd</i>	0+3×542.	971	2202		<i>vwd</i>	
438	1669		<i>msd</i>	0+(672)+995.	999	2230		<i>vwd</i>	
491	1722		<i>wd</i>	0+2×864.	37 026	2257		<i>wd</i>	
* 514	1745	<i>w</i>		0+3×581.	069	2300		<i>md</i>	0+(139)+4×542.
539	1770		<i>msd</i>	0+(139)+3×542?	151	2382		<i>md</i>	0+3×995—601?
* 569	1800	<i>w</i>		0+2×899.	209	2440		<i>md</i>	
* 579	1808	<i>vw</i>			226	2457		<i>wd</i>	
622	1853		<i>md</i>	0+995+864.	268	2499		<i>wd</i>	
669	1900		<i>vwd</i>		309	2540		<i>md</i>	0+542+2×995.
682	1913		<i>msd</i>	0+2×542+995—164.	394	2625		<i>md</i>	0+3×542+995.
697	1928		<i>msd</i>		* 494	2725	<i>w</i>		0+2×864+995.
704	1935		<i>wd</i>	0+2×968; 0+2×995—59.	* 583	2814	<i>m</i>		
739	1970		<i>vw</i>		599	2830		<i>md</i>	
760	1991		<i>m</i>	0+2×995.	672	2903		<i>md</i>	0+3×968.
847	2078		<i>std</i>	0+2×542+995; 0+(672)+542+864.	758	2989		<i>wd</i>	0+3×995.
* 885	2116	<i>msd</i>	<i>wd</i>	0+(672)+542+899.	836	3067		<i>msd</i>	0+2×542+2×995
904	2135		<i>vwd</i>	0+(139)+2×995.	*38 374	3605	<i>mw</i>		0+3×542+2×995.

NOTES: Intensities are roughly estimated from plates taken under the stated conditions. Those from the paper of Henri and Angenot (denoted by H-A) have been adjusted to our scale. The letters have the following meaning: *ew*—extremely weak, *vw*—very weak, *w*—weak, *mw*—medium to weak, *m*—medium, *msd*—medium to strong, *std*—very strong, *d*—diffuse. Numbers in italics mean 1—1 transitions. Brackets indicate that the separation from the 0—0 band cannot satisfactorily be given in terms of vibrational frequencies. Asterisks indicate bands measured by Henri and Angenot only. Doubtful assignments are denoted by a question mark.

unlike these, the nitrogen atom in pyridine replaces a whole CH group whereas in the mono-derivatives only the outer H atom is substituted. This should result in an intensification of the pyridine spectrum over that of benzene itself. On the other hand, the electronic structure of pyridine is much like that of benzene because the  $\pi$  electrons still have  $D_{6h}$  symmetry. Hence pyridine should “remember” the spectroscopic characteristics of benzene, namely, a weak absorption system forbidden by symmetry but made allowed through interaction of a vibration of suitable symmetry. Indeed, the maximum molar extinction coefficient of pyridine<sup>4</sup> (in hexane solution) is only about 10 times as great as that of benzene. This is of the same order of magnitude as the intensification in phenol and aniline absorption. It was therefore interesting to analyze the pyridine spectrum with a comparison of the benzene spectrum in mind.

<sup>4</sup> C. W. F. Spiers and J. P. Wibaut, Rec. Trav. Chim. Pays-Bas 56, 573 (1937).

If we assume that we can treat the pyridine molecule as a substituted benzene, then the levels between which the near ultraviolet transition takes place will have the symmetry which the benzene levels acquire upon transformation from  $D_{6h}$  symmetry to  $C_{2v}$  symmetry. Thus the pyridine spectrum should represent an  ${}^1A_1-{}^1B_1$  transition. The essential symmetry elements, which refer to electronic and vibrational levels as well, are given in Table II. As usual,  $C_{2v}$  denotes a twofold axis in the molecular plane passing through the nitrogen atom and  $\sigma_z$  denotes the molecular plane. The + and — signs indicate symmetrical and antisymmetrical behavior when symmetry operations with respect to these elements are performed. The ground state of the pyridine molecule is totally symmetrical, i.e.,  $A_1$ . It can be seen from Table II that the transition  $A_1-B_1$  is allowed with a transition moment lying in the molecular plane perpendicular to the CN axis in the  $x$  direction. Since the transition moment  $M$  has the transformation properties of

a translation, denoted as  $T$ , it can also be seen from Table II that the product  $A_1B_1M_y = A_1B_1A_1$  contains  $B_1$  and that the product  $A_1B_1M_z = A_1B_1B_2$  contains  $A_2$ . Hence excitation of vibrations of type<sup>5</sup>  $\beta_1$  and  $\alpha_2$  may bring out the  $y$  and  $z$  components of the electric moment, otherwise forbidden. Column 5 contains the selection rules for Raman and infra-red spectra. Column 6 indicates how many of the 27 possible pyridine vibrations belong to the different symmetry classes.

We may summarize briefly: we expect the pyridine spectrum to have the characteristics of an allowed transition, but keeping in mind that because of the resemblance of the electronic structures in pyridine and benzene the absorption strength will not be much greater than that of benzene. The 0,0 band should be among the strong bands. Bands resulting from excitation of totally symmetric vibrations will make up the main part of the spectrum. In addition, a number of weak bands may occur which correspond to the  $y$  and  $z$  components of the electric moment made allowed through interaction of vibrations  $\beta_1$  and  $\alpha_2$ .

From these remarks it would seem that the pyridine spectrum should have much resemblance to the corresponding spectra of simple substituted benzenes of symmetry  $C_{2v}$  and that the analysis could be carried through in close analogy to the analyses of these spectra. However, the appearance of the pyridine spectrum reveals at once characteristic differences from the spectra of the monohalogenated benzenes or of phenol, for example. In one respect it is even different from any of the substituted benzene spectra: while the bands of these spectra show pronounced degradation to the red, this is not the case with the pyridine bands. We will take up the matter of the structure of the individual bands in a later section and first discuss the other differences which concern the vibrational structure of the spectrum.

#### OCCURRENCE OF RING VIBRATIONS

We have taken the strong band at  $34769\text{ cm}^{-1}$  as the 0-0 band of the pyridine spectrum,

<sup>5</sup> If the symbol refers to the symmetry character of a vibrational instead of an electronic level, small Greek letters are used.

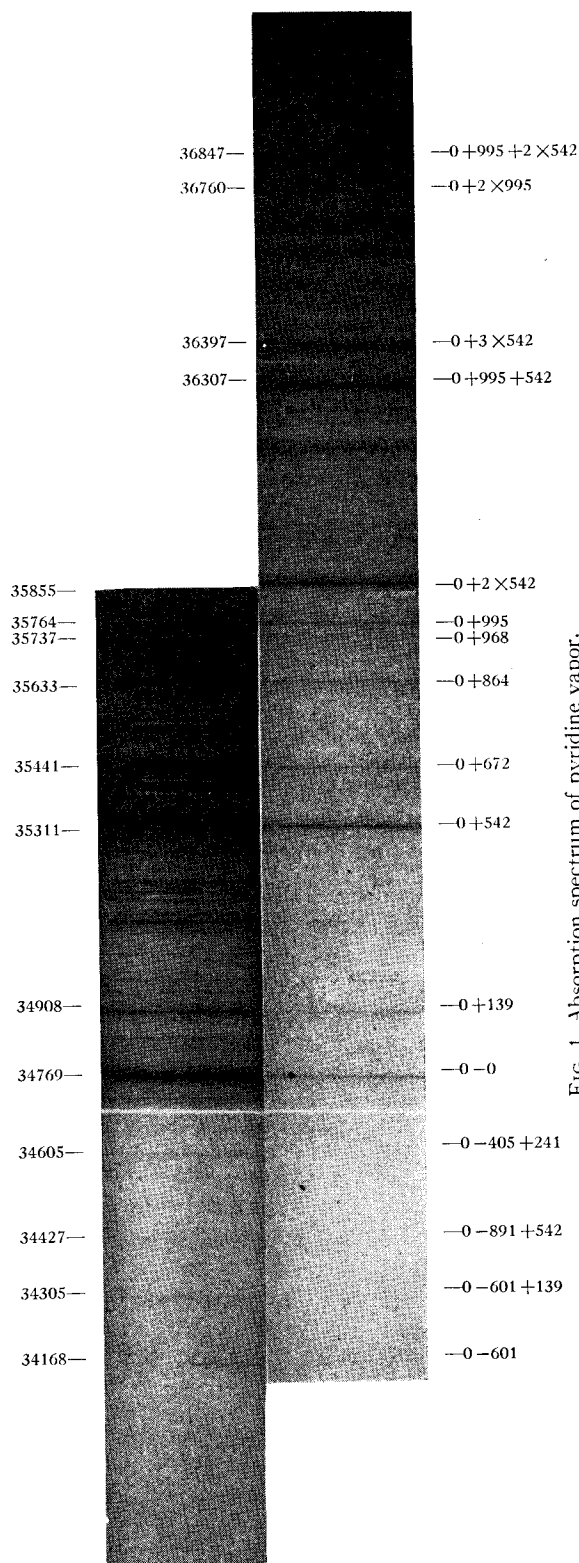


FIG. 1. Absorption spectrum of pyridine vapor.

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

Symmetry class	Essential symmetry elements $C_2^y$	$\sigma_z$	Transl.	Selection rules Raman	Infra-red	Number of vibrations
$A_1$	+	+	$T_y$	$p$	$a$	10
$A_2$	+	—		$dp$	$ia$	3
$B_1$	—	+	$T_x$	$dp$	$a$	9
$B_2$	—	—	$T_z$	$dp$	$a$	5

whereas Henri and Angenot had considered the band  $35762\text{ cm}^{-1}$  as the origin of the system. Their formulas representing five progressions contain five different ground state frequencies and one upper state frequency. The progressions include bands coming from high vibrational levels in the ground state. Some of the given intensities seem too large for the corresponding Boltzmann factors. For example, the band  $34336$  which appears at  $63^\circ\text{C}$  at a pressure of  $59\text{ mm}$  in a  $40\text{-cm}$  tube with an intensity  $45$  (given intensity  $45$  means  $100/45=2.0\text{ mm}$  is the pressure at which the band would appear in a  $100\text{-cm}$  tube) is interpreted as  $35762+4\times 542-6\times 600$ . This means that  $6$  quanta of  $600\text{ cm}^{-1}$  are excited in the ground state. The Boltzmann factor for the excitation of one quantum of  $600\text{ cm}^{-1}$  is about  $0.05$ , that of  $6$  quanta about  $4\times 10^{-7}$ . Another band  $37023$ , which appeared in  $100\text{-cm}$  layer at a pressure of  $0.86\text{ mm}$  at  $18.5^\circ\text{C}$  with an intensity  $1000$ , was interpreted as  $35762-1144-5\times 600+10\times 542$  giving a Boltzmann factor of  $2\times 10^{-9}$ . It was mainly the difficulties in reconciling some Boltzmann factors with the given interpretations and the occurrence of irregularities in the intensity distribution within the progressions which called for a new analysis. We have shifted the  $0-0$  band to longer waves, and we have used for the analysis many Raman and infra-red vibrations in the lower and upper states. Although we also have small Boltzmann factors for a number of bands, yet they do not seem incompatible with the observed intensities. For example, the weak band  $33551$  which involves the excitation of  $1218\text{ cm}^{-1}$  in the normal state gives, at a temperature of  $32^\circ\text{C}$ , a Boltzmann factor of  $2\times 10^{-3}$ . Another band at  $32520\text{ cm}^{-1}$ , measured by the French authors and resulting from the simultaneous excitation of the vibrations  $1218$  and  $1031$  in the ground state, gives a Boltzmann factor of  $2.0\times 10^{-3}$  for the used temperature of  $308^\circ\text{C}$ .

Progressions involving the excitation of totally symmetrical carbon vibrations in the  $1000\text{-cm}^{-1}$  frequency region appear with only medium intensity while they represent the strongest bands in benzene and benzene derivative spectra. We interpret the bands  $35737$  and  $35764\text{ cm}^{-1}$  as transitions from the vibrationless<sup>6</sup> ground state to singly excited symmetrical carbon ring vibrations in the upper electronic state. The values in the ground state are known from Raman spectra<sup>7-12</sup> and infra-red spectra<sup>13-15</sup> as  $1028$  and  $990\text{ cm}^{-1}$ . The values in the excited state are  $995$  and  $968\text{ cm}^{-1}$ , respectively. Both vibrations form progressions which, although strong at higher pressures, do not stand out as clearly as do the corresponding progressions in the substituted benzenes or in benzene itself. The  $995$  progression is the stronger of the two.

As in the monohalogenated benzenes there should be in pyridine another symmetric carbon ring vibration not far from the discussed frequency range. Indeed, a Raman line has been reported at  $1485$  which is considered as the symmetric component resulting from the splitting of the  $1485\text{ cm}^{-1}$  in benzene. The other component is probably a little lower and has been assigned to the strong infra-red band<sup>12,16</sup> at  $1440\text{ cm}^{-1}$ . We have not been able to assign definite frequencies to these vibrations in the excited state. While we have observed the vibrations  $1028$  and  $990$  (ground state) in absorption our temperature range did not allow observation of bands resulting from high frequency vibrations in the lower state but Henri and Angenot have measured a very weak band displaced by  $1491\text{ cm}^{-1}$  to the red from the  $0-0$  band.

<sup>6</sup> We call the unexcited ground state with its zero-point vibrations the vibrationless state for simplicity's sake.

<sup>7</sup> R. Ananthakrishnan, Proc. Ind. Acad. **3**, 52 (1936).

<sup>8</sup> P. Krishnamurti, Ind. J. Phys. **6**, 543 (1931).

<sup>9</sup> K. W. F. Kohlrausch and A. Pongratz, Ber. d. d. chem. Ges. **67**, 1465 (1934).

<sup>10</sup> C. S. Venkateswaran, Phil. Mag. **15**, 263 (1933).

<sup>11</sup> K. W. F. Kohlrausch, Zeits. f. physik. Chemie **B30**, 305 (1935).

<sup>12</sup> E. Herz, L. Kahovec, and K. W. F. Kohlrausch, Zeits. f. physik. Chemie **B53**, 124 (1943).

<sup>13</sup> W. W. Coblentz, *Investigations of Infrared Spectra* (Washington, D. C., Carnegie Institute, 1905), Part I, pp. 96, 145, 272, 274, and insets.

<sup>14</sup> J. Lecomte, J. de phys. et rad. **9**, 512 (1938).

<sup>15</sup> J. Turkevich and P. C. Stevenson, J. Chem. Phys. **11**, 328 (1943).

<sup>16</sup> Ch. H. Kline and J. Turkevich, J. Chem. Phys. **12**, 300 (1944).

The most characteristic feature of the pyridine spectrum, noticed and stressed by all observers, is a progression with separations of  $542\text{ cm}^{-1}$ . A frequency of  $500\text{--}520\text{ cm}^{-1}$  has been found also in the substituted benzene spectra but there are no pronounced progressions with separations of this frequency. In fact, the occurrence of bands with the single excitation of the 500 frequency in these spectra was explained by a forbidden transition with the moment in the  $y$  direction made allowed through the interaction of this particular vibration.<sup>17</sup> It is the analog to the vibration, the excitation of which is necessary for the production of the benzene spectrum. It is true that bands, which very probably correspond to two- and perhaps threefold excitations of this vibration, appear in brom-, chlor-, and fluorbenzene<sup>18</sup> but they are weaker or much weaker than the band with the single excitation, and the bands caused by twofold excitations seem to have a structure different from that of the band resulting from the excitation of one quantum. If a similar explanation were correct for pyridine, the intensity of the 542 progression should be less than that of the progressions involving the symmetrical carbon vibrations in the  $1000\text{ cm}^{-1}$  region, and the intensity should fall off very rapidly. In reality, the 542 progression is the strongest in the spectrum and at least 4 members of it have been observed with certainty. This indicates that the progression does not represent a forbidden transition. We therefore interpret the  $542\text{-cm}^{-1}$  frequency in the excited state as the symmetric component  $\alpha_1$  which results for symmetry  $C_{2v}$  from the splitting of the  $606\text{ cm}^{-1}$  benzene vibration. Its value in the ground state is known from the Raman line  $604\text{ cm}^{-1}$  while we find  $601$  from the absorption spectrum (band  $34168\text{ cm}^{-1}$ ). Excitations of two and three quanta of this vibration have been observed in the ground state. The 542 progression occurs in all combinations with the 995 progression. Besides these combinations involving vibrations in the upper state only, there are also present bands in which one or both vibrations are excited in the ground state. Combinations of the 542 (or  $-601$ ) with the 968 vibration are less frequent.

<sup>17</sup> H. Spöner and S. H. Wollman, *J. Chem. Phys.* **9**, 816 (1941).

<sup>18</sup> S. H. Wollman, *J. Chem. Phys.* (to be published soon).

The other component  $\beta_1$  produced in pyridine by the splitting of the  $606\text{-cm}^{-1}$  benzene vibration should have a value close to  $604$ . A fairly strong Raman line was observed at  $652\text{ cm}^{-1}$ . However, both the  $604$  and  $652$  lines are depolarized<sup>10,12</sup> and hence cannot represent the  $\alpha_1$  and  $\beta_1$  component of the  $606$  vibration. It has been suggested,<sup>12,16</sup> therefore, to consider the  $604$  as unresolved containing both components  $\alpha_1$  and  $\beta_1$ . This is not surprising because of the similar masses of benzene and pyridine. The question arises whether this is also true in the excited electronic state. If not, one should expect the band at  $35311\text{ cm}^{-1}$  ( $0,0+542$ ) to be a doublet with one component much weaker than the other. Our plates do not indicate the existence of such a doublet nor can it be derived from Henri and Angenot's measurements. We do not think that the very weak band at  $35350$  can be regarded as a component of the  $35311$  band. Hence the conclusion appears justified to consider the  $542$  as unresolved within the dispersion of our instrument. The band is broader than some other bands but that does not necessarily suggest superposition of two close bands.

From this discussion the strong intensity of the  $542$  progression appears as a result of the fact that it represents a totally symmetrical carbon vibration superposed on an allowed transition (as explained before) and also the unsymmetrical component which corresponds to the vibration which makes the electronic transition in benzene allowed.

The band  $34711\text{ cm}^{-1}$ , which is  $58\text{ cm}^{-1}$  from the  $0,0$  band, is probably the  $1-1$  transition of the discussed vibration ( $601-542=59$ ). A few other weak bands shifted by the same amount towards the red from strong bands may indicate the superposition of this  $1-1$  transition on symmetric ring vibrations. The explanation has to be given with some caution, however, because the shifted bands are not always present at the expected places.

The Raman frequency  $652\text{ cm}^{-1}$  was assigned to an out-of-plane vibration, a CH vibration by the Kohlrausch group and a ring vibration by Kline and Turkevich. The latter authors considered an interpretation as  $\beta_2$  vibration as probable, corresponding to  $\beta_{2g}$  in benzene. According to selection rules a  $\beta_2$  vibration should not



occur singly excited in the discussed absorption system. If it would appear in violation of the selection rules for  $C_{2v}$  symmetry, it should represent an extremely weak band. This is not true for the band  $34121\text{ cm}^{-1}$  displaced by  $649\text{ cm}^{-1}$  to the red from the 0,0 band and probably involving the same vibration as the Raman line 652. Superposing 542 on this band gives 34663 whereas a diffuse band has been measured at 34657 and might fit the explanation. Adding one more quantum leads to a weak band observed by Henri and Angenot. Another band at 35117 may be explained as  $0,0 - 649 + 995 = 0,0 + 346$ . Therefore, it does not seem very probable that the  $-649$  difference occurring in the ultraviolet absorption spectrum can be explained as a  $\beta_2$  vibration. Hence, the band 34121 has either a different origin or the 649 vibration must be assigned differently. We shall take up these questions later again in connection with the assignment of hydrogen vibrations.

It is plausible to consider the band 35350 as containing the corresponding vibrational transition of the 649 in the upper state. This gives a value of  $581\text{ cm}^{-1}$  for this vibration. The band is weak, so are the bands 35889 and 36341 resulting from superpositions of 542 and 995 on the 35350 band.

The  $\epsilon_u^+$  benzene ring vibration of  $406\text{ cm}^{-1}$  splits in pyridine into the components 374 and  $404\text{ cm}^{-1}$ . In benzene strong bands were found on the long wave-length side of all prominent bands at a distance of  $160\text{ cm}^{-1}$  which was explained as resulting from a 1-1 transition of this vibration. Assuming a similar behavior in pyridine we tentatively interpret the band 34605 ( $-164$  from the 0,0 band) as 1-1 transition of the 404 component. As may be seen from Table I bands can be found displaced by 164 to the red from 35311 ( $1 \times 542$ ), 35855 ( $2 \times 542$ ), 36397 ( $3 \times 542$ ) and from combination bands of the 542 and 995 progressions. Strangely enough they do not occur as companions of the 995 bands alone. This is one of the numerous little puzzles still present in the spectrum. The band 34003 ( $-766$  from 0,0) fits the interpretation  $-601 - 164 = -765$ .

Henri and Angenot report two very weak bands at 34391 and 34364 displaced to the red from the 0,0 band by 378 and 405, respectively. It is quite possible that these separations correspond to the

Raman lines 374 and  $404\text{ cm}^{-1}$ . The symmetry type of these vibrations is  $\beta_2$  and  $\alpha_2$ , respectively.<sup>12,16</sup> The single excitation of a  $\beta_2$  vibration is forbidden in our absorption system while the single excitation of an  $\alpha_2$  vibration produces a transition moment perpendicular to the molecular plane. We have an indication of the 404 band on some plates but were unable to locate the 374 band. Using 405 and the difference 164, a value of  $241\text{ cm}^{-1}$  is obtained for the vibration in the upper state. Twofold excitations of 405 and 241 lead to allowed transitions. Indeed, the band 33957 observed by the French authors may be interpreted as  $-2 \times 405$ .

It should be mentioned that the medium strong band 34908 fits the explanation  $0,0 + 542 - 403 = 0,0 + 139$  but it is hard to believe that the combination of an  $\alpha_1$  and an  $\alpha_2$  vibration produces a band of the observed intensity, particularly when the transition 0,0-403 is practically absent. A 542 progression can be built up on the 139 band and subtracting 601 from it leads to another prominent band. We shall discuss this band later again.

In the search for an occurrence of the 1-1 transition of the 374 vibration we only found a weak band at 34618 observed by Henri and Angenot and displaced by  $-151$  from the 0,0 band. Using 378 from the ultraviolet absorption spectrum  $226\text{ cm}^{-1}$  obtains for this vibration in the upper state. Bands can be found in the places  $0,0 - 2 \times 151$ ,  $0,0 - 2 \times 378$ ,  $0,0 + 2 \times 226$ , but subtraction of 151 from the strongest bands leads to new bands in a very few instances only. We emphasize that the suggested scheme of the 151 difference must be considered as very tentative.

#### OCCURRENCE OF HYDROGEN VIBRATIONS

The identification of hydrogen vibrations in the spectrum of pyridine is of particular interest since, with a few exceptions, their appearance could not be proved unambiguously in the absorption spectra of benzene and its derivatives. An examination of pyridine plates taken at high pressures reveals at once the presence of many bands on the long wave-length side whose separations from the 0,0 band coincide with Raman lines and infra-red bands, and which cannot be explained as ring vibrations or combinations of such. Omitting separations resulting

from ring vibrations, the following frequency values in  $\text{cm}^{-1}$  denote such separations on the long wave-length side from the 0,0 band: 345, 395, 464, 649, 868, 891, 945, 1063, 1218. Weaker bands appear at distances of 678, 712, 1141, and some very weak bands at 1372 and at higher values. The differences 712, 891, 945, 1063, 1218, 1141, 1372 agree with frequencies observed in the Raman and infra-red spectrum. Assignments of these frequencies to modes of vibration have been offered by Kohlrausch and co-workers, and by Kline and Turkevich. Both groups consider them as hydrogen vibrations, but disagree in the individual interpretations. Their proposals for the hydrogen bending vibrations are collected in Table III.

The bands  $-891$ ,  $-945$ ,  $-1063$  and  $-1218$  are all of similar intensity. The respective separations appear also in other bands in conjunction with the symmetric ring vibrations 542, 968, 995 in the upper and 601, 992, 1031 in the lower state. Furthermore, they combine with each other and with other hydrogen vibrations. The close agreement of the four separations with Raman and infra-red frequencies suggests that they represent fundamental vibrations. However, a detailed discussion of the experimental data will require some modification of this conclusion.

When studying the spectrum of pyridine two characteristic pairs of bands are easily spotted: the strong pair 0,0 and  $0+139$  and the weaker pair  $0-601$  and  $0+139-601 = -462$  (see Fig. 1). A third still weaker pair is found shifted by another  $601 \text{ cm}^{-1}$  towards longer waves:  $0,0-2 \times 601$  and  $0+139-2 \times 601$ . The separations of these bands from the 0,0 band are  $-1202$  and  $-1202+139 = -1063$ . Henri and Angenot have observed even a fourth pair of extremely weak bands when moving another  $601 \text{ cm}^{-1}$  to the red. As discussed in the preceding section the 601 is the frequency value of a symmetric carbon vibration. If now the meaning of the separation  $+139$  would be known, all bands of the different pairs would be explained at once. The 139 band will be discussed later in some other connection but it may be stated at this place already that it is one of the few bands for which a satisfactory explanation cannot be offered at present. Assuming for the moment that the  $+139$  band be explained, then the  $-1063$  band would represent a transi-

tion in which two vibrational levels of the 601 vibration are excited in the ground state on top of the vibrations already involved in the  $+139$  band. If the  $-1063$  band contains also the excitation of the hydrogen vibration  $1061 \text{ cm}^{-1}$ , the intensity ratio between the bands  $-1202$  and  $-1063$  should differ from that of the bands  $-601$  and  $-464$ , for example. Indeed, the first two bands are of similar intensity while the intensities in the second pair are about 2:1. Hence it may be concluded that the  $-1063$  band represents a superposition of the two transitions. We have noticed that the 1063 frequency, besides combining with 601, occurs also in superposition with 542 and  $2 \times 542$  but not with 995 and 968 nor with the corresponding vibrations in the ground state. The assignments of 1063 to a vibrational type (from Raman and infra-red data) are shown in Table III. Although the ultraviolet data do not permit a definite decision between the two propositions, an interpretation as  $\alpha_1$  or  $\beta_1$  vibration is more probable from our point of view since excitation of an  $\alpha_2$  vibration is very likely connected with a very small transition probability. It is not impossible that the diffuse band 35786 corresponds to the excitation of the discussed vibration in the upper state ( $1017 \text{ cm}^{-1}$ ) although Table I gives also an alternative explanation, but different transitions involving the same energy are not infrequent.

The  $-891$  separation can likewise be explained in a twofold way. First, it may be noticed that it is displaced by  $+139$  from the  $-1031$  band and hence may be a combination of the  $+139$  separation and the carbon ring vibration 1031. Although the intensity ratio of  $-1031:-891$  as taken from Henri and Angenot's paper is about 2:1, we think that excitation of the CH vibration  $884 \text{ cm}^{-1}$  (average value from Raman and infra-red data) is partly responsible for the band. This may be concluded from the fact that more superpositions of ring and hydrogen vibrations can be found on the  $-891$  band than on any other band on the long wave-length side from the 0,0 band. Of the two suggestions (Table III), to assign the frequency  $884 \text{ cm}^{-1}$  to an  $\alpha_1$  or  $\alpha_2$  vibration we prefer the first, but regard an interpretation as  $\beta_1$  vibration also as possible. The band at 35633 with a separation of 864 from the 0,0 band is tentatively considered as repre-

TABLE III. Hydrogen bending vibrations in pyridine.

	In the molecular plane						Perpendicular to the molecular plane					
Type in $D_{6h}$	(3) $\alpha_{2g}$	(15) $\beta_{2u}$	(9) $\epsilon_g^+$	(18) $\epsilon_u^-$			(11) $\alpha_{2u}$	(5) $\beta_{2g}$	(10) $\epsilon_g^-$	(17) $\epsilon_u^+$		
Type in $C_{2v}$	$\beta_1$	$\beta_1$	$\alpha_1$	$\beta_1$	$\alpha_1$	$\beta_1$	$\beta_2$	$\beta_2$	$\alpha_2$	$\beta_2$	$\alpha_2$	$\beta_2$
Kohlrausch <i>et al.</i>	1370	1290	1218	1139	1069	<i>m</i>	<i>m</i>	747	890	652	710	
Kline and Turkevich	1210	1139	1139	<i>m</i>	884	1037	669	941	747	710	1063	<i>m</i>

Numbers in brackets in the first row refer to Wilson's numerical notation. *m* = missing denotes hydrogen vibrations which disappear in pyridine as compared to benzene.

senting the discussed vibration in the excited electronic state. The 542 and 995 appear superposed on it and  $2 \times 864$  has also been observed.

No double interpretation seems possible for the  $-1218$  and  $-945$  bands. A medium strong Raman line with a depolarization factor between 0.6 and 0.75 was found at  $1218 \text{ cm}^{-1}$ . The frequency occurs also in the infra-red. From this an assignment was suggested to a bending vibration in the molecular plane, namely a  $\beta_1$  vibration (Kline and Turkevich) or an  $\alpha_1$  vibration (Kohlrausch and others). Both explanations are compatible with the relatively strong intensity of the  $-1218$  ultraviolet absorption band. No preference can be derived from ultraviolet absorption data. Adding 542 to  $-1218$  obtains  $-676$  which explains another of the mentioned separations. It is not impossible that part of the intensity of the  $-676$  band is caused by the superposition of a fundamental vibration suggested by Turkevich and Stevenson as  $669 \text{ cm}^{-1}$  from infra-red data. It is not certain whether the band  $35944$  or the band  $35953$  can be interpreted as transition to the single excitation of the  $1218$  in the upper state. If so, the corresponding frequency would be  $1175$  or  $1184 \text{ cm}^{-1}$ . Superpositions of 542 and 995 on  $1175$  or  $1184$  fall close to or on top of other more likely transitions.

The fundamental frequency  $941 \text{ cm}^{-1}$  is known from a very weak Raman line and from an infra-red band observed with medium intensity in the vapor spectrum. Kline and Turkevich assign it to a  $\beta_2$  vibration resulting from the benzene vibration  $\beta_{2g}$ . It is very difficult to reconcile the intensity of the ultraviolet band  $-945$  with this interpretation. In fact, the intensity of this band would suggest rather an  $\alpha_1$  or  $\beta_1$  vibration. A number of bands may be explained by superposing on  $-945$  the ring vibrations in the  $1000\text{-cm}^{-1}$  region and the  $-601$  difference; there are also combinations of 945 with other hydrogen

vibrations. But it is peculiar that a  $542$  progression cannot be built up on it.  $-945 + 542$  gives a separation of  $-403$  from the  $0,0$  band. There is an extremely weak band at this location which we have interpreted before as resulting from the excitation of an out-of-plane carbon ring vibration. The band  $34374$ , which is of an intensity comparable to that of the  $-945$  band, is displaced by only  $-395$  from the  $0,0$  band. No satisfactory interpretation of this difference can be offered in terms of other frequencies. However, superposing  $2 \times 542$  on  $-945$  leads to the strong band  $+139$  with an intensity too strong for the Boltzmann factor of a  $945\text{-cm}^{-1}$  vibration. Actually, this band appears almost simultaneously with the  $0,0$  band and hence must have a different origin. To explain it as resulting from a  $1-1$  transition is not a likely possibility. The vibration would have, contrary to the rule, a larger frequency in the excited than in the normal state, and because of the intensity of the band, it would have to be a low vibration. Not only would  $139 \text{ cm}^{-1}$  then be a relatively large change but it cannot obviously be connected with any of the few low frequency vibrations. Adding 542 on 139 gives again a strong displaced band ( $35441$  instead of  $35450$ , in Table I the separation of  $35441$  from the  $0,0$  band is used as (672)). The succeeding member is regular and weak. Attempts to explain the first displacement as caused by resonance with the 405 vibration lead to difficulties because of group theoretical selection rules. If 945 represents a  $\beta_1$  and 405 an  $\alpha_2$  vibration resonance should not take place. If they were both of type  $\alpha_2$  resonating interaction would be possible between 405 and  $-945 + 542$ . But in this case 945 should not occur in the infra-red whereas Turkevich and Stevenson report a medium strong band in the vapor. Also the intensity of the ultraviolet band  $-945$  is high for an  $\alpha_2$  vibration. We feel that we should point out

TABLE IV. Pyridine vibrations occurring in ultraviolet absorption.

	Carbon ring vibrations						Hydrogen vibrations								
Lower state	1485	1031	992	[649]	601	405	1372?	1218	1139	1063	945	891	712	676?	[649]?
Upper state		995	968	[581]?	542	241?		1175? or 1184?		1017?	899?	864?			[581]?
Type	$\alpha_1$	$\alpha_1$	$\alpha_1$	?	$\alpha_1$	$\alpha_2$	?	$\beta_1$	$\alpha_1$ or $\beta_1$	$\alpha_1$ or $\beta_1$	$\beta_1$	$\alpha_1$ or $\beta_1$	?	?	?

[ ] means uncertainty as to ring or hydrogen vibration.

these difficulties but we must admit that we cannot offer a convincing solution of them at present.<sup>19</sup> The frequency of the 945 vibration in the upper state is very tentatively suggested as 899  $\text{cm}^{-1}$  calculated from the weak band 35668. Addition of 995 leads to a band of similar intensity,  $2 \times 899$  gives a band of double intensity. Superpositions of 542 could not be found.

There remain the differences 712, 1141, 1372 which agree also with Raman and infra-red frequencies. The band 34057 with a separation of 712 to the red from the 0,0 band is very weak. This separation may correspond to the medium strong infra-red band 710  $\text{cm}^{-1}$  which has been explained as  $\beta_2$  from  $\epsilon_g^-$  or  $\epsilon_u^+$ . Kline and Turkevich assume the other component  $\alpha_2$  from  $\epsilon_g^-$  at 747  $\text{cm}^{-1}$  whereas Kohlrausch and co-workers prefer an assignment to  $\beta_2$  coming from  $\beta_{2g}$ . (See Table III.) A fundamental frequency of 747  $\text{cm}^{-1}$  is not present in the ultraviolet absorption spectrum. We have not been able to settle without ambiguity the question of the nature of the 712 and 747 frequencies.

The 1141 difference represents a weak band and corresponds probably to the Raman and infra-red band 1139 which was interpreted as symmetric component originating mainly from  $\epsilon_g^+$ . The 1141 difference occurs combined with -601 and 542.

The infra-red band 1374 was tentatively assigned to a  $\beta_1$  vibration by the Kohlrausch group

<sup>19</sup> It would be interesting to investigate the absorption of  $\alpha$ -picoline (2-methyl-pyridine  $\text{C}_5\text{NH}_4\text{CH}_3$ ) which is a likely impurity. But although our purification method was not extreme, such impurity bands should occur with very small intensity only. Henri and Angenot mention in their paper that they have photographed the  $\alpha$ -picoline spectrum and they would have noticed coincidences in both spectra. Unfortunately, their results on  $\alpha$ -picoline have evidently not been published. Earlier investigation by E. Herrmann, Zeits. f. wiss. Phot. 18, 253 (1919).

but considered as combination or impurity by Kline and Turkevich. In ultraviolet absorption it shows up in an extremely weak band (33397  $\text{cm}^{-1}$ ). Both possibilities are mentioned in Table I.

Before concluding the section on hydrogen vibrations we should take up once more the question of the origin of the 649 difference. The corresponding Raman line was assigned by the German authors to the optically inactive component, i.e.,  $\alpha_2$ , of the  $\epsilon_u^+$  CH vibration in benzene. They remark that the intensity of the line is unusually high for this interpretation. The fact that since then Turkevich and Stevenson<sup>15</sup> located a medium strong band at 650  $\text{cm}^{-1}$  in the infra-red vapor spectrum and the fair intensity of the corresponding ultraviolet band render the interpretation as  $\alpha_2$  doubtful. Because of these and other difficulties mentioned before, no assignment is suggested for this frequency difference at present.

Reviewing our results in comparison with those from Raman and infra-red spectra we found agreement on the interpretation of most ring vibrations but deviations in the interpretation of hydrogen vibrations. We made some effort to find an unambiguous set of hydrogen bending vibrations which will satisfy the results of all three spectra. This could not be achieved. It seemed preferable, therefore, to tabulate separately (Table IV) the vibrations which occur in ultraviolet absorption and to indicate their vibrational type as suggested from the ultraviolet spectrum without correlating the types with those of the benzene vibrations.

#### APPEARANCE OF INDIVIDUAL BANDS

While benzene and the known substituted benzene spectra show pronounced degradation of

the bands to the red, most pyridine bands have a line-like appearance. Although they too have edges on the violet side with a very narrow shading toward the red, a number of them show also fuzziness on the violet side of the edge. Under suitable pressure conditions fine structure can be distinguished in this fuzziness in some bands, as in the 0,0 band at  $34769\text{ cm}^{-1}$ , the first two members of the 542 progression and a few others. The extension of the fuzzy region is larger on the violet side than on the red side, but both never become as pronounced as the shading (to the red) in the substituted benzene spectra. Superficially the bands look like more or less broad lines with a sharper edge on the violet side and at higher pressures they are accompanied by narrow continuous regions (which broaden with pressure) on either side.

Such a structure might be understood if the moments of inertia are very nearly the same in both the lower and upper states. Considering in first approximation the pyridine molecule as a symmetrical top like the benzene, its rotational energy can be represented by

$$E_r = \frac{\hbar^2}{2A} [2J(J+1) - K^2],$$

where  $A$  is the principal moment of inertia about the  $z$  axis (perpendicular to the molecular plane). The main branches  $P$ ,  $Q$ , and  $R$  are determined by  $\Delta J = -1, 0, +1$ . If  $A'$  and  $A''$  (moments of inertia in upper and lower state) are approximately equal, the lines of the  $Q$  branch fall nearly in the

same place ( $\nu_0$ ). The  $Q$  branch is then intense and narrow while the heads of the  $P$  and  $R$  branches (in our case  $R$  branch) lie, for  $A' = A''$ , at some distance from the zero line or the  $Q$  branch. This distance from the origin may be so great that for the corresponding  $J$  value the intensity of the lines may have fallen off so much to be too weak for observation. This would account satisfactorily for the fact that a number of bands look as if degraded to both sides with an intense head in the middle. That in some bands an indication of structure can be seen on the violet side may be explained by assuming non-overlapping of the  $R$  branch on this side by the  $Q$  branch. This may account partly for the different extension of the fuzzy regions. Superimposed on this coarse structure is the  $K$  structure. Much narrower  $p$  and  $r$  branches according to  $\Delta K = \pm 1$  or narrow  $q$  branches according to  $\Delta K = 0$  occur superimposed on the main  $P$ ,  $Q$ , and  $R$  branches. The bands  $\Delta K = \pm 1$  correspond to changes of the transition moment in the  $x$ ,  $y$  directions and the bands  $\Delta K = 0$  to a change in the  $z$  direction. It is of course hopeless to observe the  $K$  structure, even with very large dispersion. In spite of this we know that most bands belong to the type  $\Delta K = \pm 1$  because the vibrational analysis has revealed that in all strong bands the transition moment lies in the molecular plane.

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