Near Ultraviolet Absorption Spectrum of Pyridine-d_5 Vapor

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The near ultraviolet absorption spectrum of pyridine-d_5 vapor due to n–π^* transition was measured and analyzed. The origin is at 34951 cm^{-1} and higher than that of pyridine-h_5 by 182 cm^{-1}. The ground-state frequencies 582 and 1019 cm^{-1} and their counterparts of 511 and 953 cm^{-1} in the upper state dominate the progressions in the spectrum. Besides the above frequencies, several active frequencies were obtained.

The near ultraviolet absorption spectrum of pyridine-h_5 vapor has been observed by Henri and Angenot$^{1)}$ and by Sponer and Stücklen.$^{2)}$ Assuming that the electronic transition is polarized in the molecular plane perpendicular to a twofold axis passing through the nitrogen atom, Sponer and Stücklen have assigned many bands in the region to the progressions with several totally and nontotally symmetric frequencies. In the spectrum of Sponer and Stücklen, the origin and the progressional members with the totally symmetric frequencs 542 cm^{-1} have been observed to belong to the parallel bands of an oblate symmetric top. The electronic transition has, therefore, been assigned to the A_1–B_1 transition with the electronic transition moment perpendicular to the molecular plane.$^{3)}$ Although Sponer and Stücklen have reported on several fundamental frequencies in the ground and upper states, ambiguity remains on the character of the vibrations.

The infrared and Raman spectra of pyridine and deuteropyridines and their vibrational analyses have been extensively studied by many workers.$^{3-7)}$ Their works provide us with much information on the n–π^* absorption spectrum of pyridine.

The purpose of the present study is to analyze the n–π^* absorption spectrum of pyridine-d_5 vapor in relation to that of pyridine-h_5 vapor.

Experimental

The spectrum was photographed in the second order of a Shimadzu GE-100 Ebert type grating spectrograph with a 500 W xenon arc lamp as light source. The reciprocal dispersion was 4.1 Å/mm. A Toshiba UV-D2 filter was used to eliminate all radiation in the other orders. Fuji spectroscopic plates were used. The wavelengh calibration was made by an iron arc. The absorption cells with quartz windows had light path lengths 20 and 60 cm. The 20 cm cell had a side arm in which the sample was kept during exposures at temperatures varying from −16°C to room temperature. The 60 cm cell into which the sample was introduced was helically wound with nichrome wire over an asbestos sheet and covered with an asbestos sheet. The cell temperature could be regulated between room temperature and 50°C.

The 99% pure pyridine-d_5 was a Merk product. The sample was twice distilled in a vacuum and then introduced into the absorption cell in a vacuum. The spectrum of pyridine-d_5 showed no spectrum of pyridine-h_5.

Results and Discussion

The n–π^* absorption bands of pyridine-d_5 vapor observed at −16°C appear in the wavelength region 2860—2620 Å. The bands have narrow line-like shapes in the longer wavelength region, but become diffuse in the shorter wavelengths and finally are submerged in a strong continuum. The strongest band at 34951 cm^{-1} in the longest wavelength region is taken as the origin, which is shifted by 182 cm^{-1} toward the blue compared

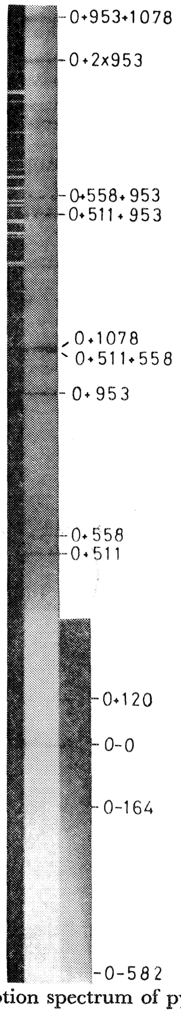

Fig. 1. Absorption spectrum of pyridine-d_5 vapor.

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6) D. B. Cunliffe-Jones, *Spectrochim. Acta*, **21**, 747 (1965).

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Table 1. Absorption bands of pyridine-d_5

Wave number	Separation from origin	Intensity		Assignment
		tube 60 cm		
		50°C	40°C	
33353	−1598	w		0−582−1019
33473	−1478	w		0−582−1019+120
33544	−1407	w		0−582−828
33616	−1335	w		0−1335
33626	−1325	w		0−1325
33692	−1259	vw		0−582−680
33719	−1232	vw		
33788	−1163	s	m	0−2×582
33853	−1098	w		0−2×582+62
33876	−1075	w		0−1019−56
33906	−1045	m		0−2×582+120
33932	−1019	s	m	0−1019
33938	−1013		vw	
33967	−984		vw	0−1019+34
33993	−958		vw	0−958 0−1019+62
34053	−898		m	0−1019+120 0−582−(316)
34060	−891		vw	0−891
34089	−862		vw	0−1019+120+34 0−582−(316)+34
34123	−828		wd	0−828 0−1335+511
34145	−806		vw	0−1325+511
34186	−765		vwd	0−765
34202	−749		w	0−582−680+511
34205	−746		s	0−582−164
34271	−680		s	0−680
34312	−639		s	0−582−56
34329	−622		w	0−622
34338	−613		wd	
34369	−582		s	0−582
34403	−548		vwd	0−582+34
34431	−520		w	0−520 0−582+62
34445	−506		w	0−1019+511
		tube 60 cm		
		40°C	20°C	
34488	−463	s	m	0−582+120
34492	−459	vw		0−1019+558
34517	−434	vw		
34526	−425	m		0−582+120+34
34545	−406	vw		
34572	−379	w		0−1335+953
34580	−371	wd		0−371 0−1325+953
34590	−361	w		
34603	−348	w		
34621	−330	s		0−2×164
34635	−316	vs	s	0−(316) 0−828+511
34668	−283	s	m	0−(316)+34 0−828+511+34
34686	−265	md		0−828+558
34710	−241	w		0−1325+1078
34726	−225	s	w	0−1019+802 0−164−56
34743	−208	s	w	
34764	−187	s	w	0−582+558−164 0−164−20
		tube 60 cm	20 cm	
		20°C	−16°C	
34783	−168	w		0−680+511
34787	−164	s		0−164
34803	−148	vw		
34821	−130	m		0−164+34
34826	−125	w		0−680+558
34832	−119	w		
34866	−85	vw		
34882	−69	m		0−582+511
34885	−66	m		0−1019+953
34895	−56	vs		0−56
34911	−40	m		0−2×20
34931	−20	s		0−20 0−582+558
34951	0	vs	s	0−0
34985	34		vw	0+34
35013	62		w	0+62
35071	120		m	0+120 0−680+802
35127	176		vw	
35153	202		vw	
35160	209		vw	
			tube 20 cm	
			−16°C	
35192	241		vw	0+2×120
35222	271		w	0−680+953
35252	301		w	
35318	367		vw	0−582+953
35327	376		vw	
35445	494		w	0−582+1078
35462	511		s	0+511
35509	558		s	0+558
35581	630		w	0+511+120
35622	671		m	0+558+120
35732	781		w	0−680+511+953
35739	788		w	0+953−164
35753	802		vw	0+802
35770	819		w	
35783	832		w	0−680+558+953
35904	953		vs	0+953
35977	1026		vw	0+2×511
35982	1031		vw	
35999	1048		vw	
36021	1070		vs	0+511+558
36029	1078		vs	0+1078
36166	1215		w	
36183	1232		w	
36197	1246		w	

TABLE 1 (Continued)

Wave number	Separation from origin	Intensity	Assignment	Wave number	Spearation from origin	Intensity	Assignment
36260	1309	m	0+511+802	37413	2462	md	0+558+2×953
36410	1459	vs	0+511+953	37474	2523	wd	
36460	1509	vsd	0+558+953	37507	2556	wd	
36539	1588	w	0+511+1078	37560	2609	vwd	
36544	1593	w		37617	2666	vwd	
36727	1776	m	0−680+558+2×953	37665	2714	wd	0+802+2×953
36854	1903	s	0+2×953	37806	2855	md	0+3×953
36926	1975	wd	0+2×511+953	37835	2884	vwd	
36975	2024	vsd	0+953+1078	37888	2937	vwd	0+2×511+2×953
37216	2265	wd	0+511+802+953	37928	2977	md	0+511+558+2×953
37358	2407	sd	0+511+2×953	38176	3225	wd	0+511+802+2×953

Notes: Intensities are roughly estimated from plates.
Abbreviations: v=very, w=weak, m=moderate, s=strong, and d=diffuse.

TABLE 2. ACTIVE FREQUENCIES OF PYRIDINE-h_5 AND PYRIDINE-d_5 (cm^{-1})

Symmetry	Mode	Pyridine-h_5			Pyridine-d_5		
		IR, Raman[a]	Ground[b] state	Excited[b] state	IR, Raman[a]	Ground state	Excited state
a_1	1	992	992	968	962	958	
	6a	605	601	542	582	582	511
	9a	1218	1218		887	891	
	12	1029	1031	995	1006	1019	953
	18a	1068	1063		823	828	
	19a	1482	1491		1340	1335	
b_1	6b	652	649		625	622	
	14	1375	1372		1322	1325	1078
	15	1148	1141		(887)		
a_2	10a	886	891		690	680	558
b_2	4	675[c]	676?		(625)[d]		
	5	942	945		762[d]	765	
	11	703[c]	712		530	520	
	16b	405	405		371	371	

a) The values taken from Corrsin *et al.*[4]
b) The values by Sponer and Stücklen.[2]
c) Cunliffe-Jones has assigned the frequencies 700 and 746 cm^{-1} to the modes 4 and 11, respectively.[6]
d) Wilmshurst and Bernstein have assigned the frequencies 567 and 823 cm^{-1} to the modes 4 and 5, respectively.[5]

with that of pyridine-h_5.[2] With the rise of temperatures, many line-like bands appear in the longer wavelength side of the origin.

Table 1 represents our measurements with visually estimated intensities and assignments of the bands. Table 2 shows the active frequencies of the pyridine-d_5 spectrum together with those of the pyridine-h_5 spectrum.[2]

The interval 582 and 1019 cm^{-1} are most prominent in the longer wavelength region of the origin. These are identical with the frequencies 582 and 1006 cm^{-1} assigned to the totally symmetric in-plane ring bending modes 6a and 12, respectively, in the vibrational spectra.[4,5] The frequency 582 cm^{-1} corresponds to the prominent frequency 601 cm^{-1} in the pyridine-h_5 spectrum and has a counterpart of 511 cm^{-1} (542 cm^{-1} in pyridine-h_5) in the upper state. The frequency 1019 cm^{-1} has a counterpart of 953 cm^{-1} in the upper state. The frequencies 1031 and 995 cm^{-1} in the ground and upper states, respectively, in the pyridine-h_5 spectrum correspond to the frequencies.

The separation 680 cm^{-1} of the strong hot band at 34271 cm^{-1} from the origin might coincide with a frequency of 690 cm^{-1} in the vibrational spectra. This frequency is assigned to the out-of-plane hydrogen bending mode 10a with species a_2. It may be expected that the bands caused by a nontotally symmetric vibration of species a_2 show a perpendicular type.[8] The shape of the band is, however, line-like and can not be distinguished from those of the parallel bands. The frequency 680 cm^{-1} corresponds to 891 cm^{-1} in the pyridine-h_5 spectrum and has a counterpart of

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8) A. C. Albrecht, *J. Chem. Phys.*, **33**, 156 (1960).

558 cm^{-1} (probably 672 cm^{-1} in pyridine-h_5) in the upper state.

Separations 371, 520, 622, 765, and 828 cm^{-1} of weak bands to the red from the origin coincide with the respective frequencies in the vibrational spectra as shown in Table 2 and assigned as in Table 1.

Separations 891, 958, 1325, and 1335 cm^{-1} of very weak bands to the red from the origin are identical with the respective frequencies in the vibrational spectra and assigned as in Table 1.

Separation 316 cm^{-1} of the strong hot band at 34635 cm^{-1} from the origin might coincide with the frequency 329 cm^{-1} in the vibrational spectra. The analogous band separated from the origin in the pyridine-h_5 spectrum by 378 cm^{-1} is, however, extremely weak. Thus ambiguity of the band remains.

The most characteristic feature of the pyridine-d_5 spectrum is the prominence of frequency 953 cm^{-1} in the upper state. Vibration 953 cm^{-1} makes overtone bands with three members and dominates progressions in combination with other vibrations. In the pyridine-h_5 spectrum, the 542 cm^{-1} progression starting from the origin appears up to the fourth member, but the analogue of 511 cm^{-1} in pyrinine-d_5 has only two progressional members.

The other fundamental frequencies in the upper state are 558 and 1078 cm^{-1}. The frequency 558 cm^{-1} seems to make no overtone and is a counterpart of the ground-state frequency 680 cm^{-1}. The frequency 1078 cm^{-1} probably corresponds to the ground-state frequency 1325 cm^{-1}.

On both sides of the origin, satellites appear with separations −164, −56, −40, −20, 34, 62, and 120 cm^{-1}. The satellite band separated from the origin by 120 cm^{-1} corresponds to the band separated from the origin by 139 cm^{-1} in the pyridine-h_5 spectrum, which disappears from the spectrum in solid solution at low temperature.[9] This satellite might be due to a *v–v* transition of a low frequency vibration. The other satellites might be due to *v–v* transitions of some vibrations.

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[9] *Cf.* Ref. 3.