

The Vibrational Spectra of Pyrrole and Some of Its Deuterium Derivatives

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The Vibrational Spectra of Pyrrole and Some of Its Deuterium Derivatives

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The Raman spectra of pyrrole, pyrrole-*N*-*d*, symmetrical pyrrole-*d*₄, and pyrrole-*d*₅ have been studied with a high speed grating spectrograph. The infra-red absorption spectra of the same compounds have been investigated in the liquid state in the region 750–1900 cm⁻¹. With the help of the selection principles and Teller's product rule, these spectra have been analyzed for a molecule of *C*_{2v} symmetry. The analysis yields values for all but one of the twenty-four fundamental frequencies, and this one has been estimated. The spectra indicate clearly a *C*_{2v} structure for pyrrole, although a *C*_s (non-planar) structure cannot yet be rigorously excluded.

INTRODUCTION

THE pyrrole ring is of interest because it is found in many chemical substances of biological importance. In such compounds as hemoglobin, chlorophyll, the porphyrins, and several of the oxidative enzymes it is one of the chief constituents of the molecule. Our knowledge of the pyrrole molecule itself, however, is far from complete. In particular its vibrational spectra have never been analyzed, and therefore it has been impossible to establish the symmetry of pyrrole through such an analysis. The molecular symmetry must be low at best, which means that the selection rules for the vibrational spectra will not be very restrictive. Because of this lack of restriction and because of the large number of fundamental frequencies, the analysis of the vibrational spectra has not been carried very far, despite the fact that spectroscopic work on pyrrole has been extensive.

The infra-red spectrum of liquid pyrrole has been obtained twice previously.^{1,2} In the Raman effect, numerous studies of pyrrole have been made,³⁻⁹ including a careful determination of the

depolarization factors of the Raman lines by Reitz.⁸ One deuterium derivative, pyrrole-*N*-*d*, has also been studied in the Raman effect.^{10,11} It seemed to the authors that the analysis of the spectra of pyrrole might best be accomplished with the help of the spectra of the deuterium derivatives. The preparation of several of the symmetrically substituted derivatives is not difficult. We have accordingly undertaken an investigation of pyrrole, pyrrole-*N*-*d*, symmetrical pyrrole-*d*₄, and pyrrole-*d*₅ in both the Raman effect and in infra-red absorption.

EXPERIMENTAL METHODS

Preparation of the Compounds

It has been shown by Koizumi and Titani¹² that all the hydrogens in the pyrrole molecule will exchange in solutions of *pH* ≤ 1. We have confirmed and extended this work, and have found that such exchange furnishes a convenient method for preparing the symmetrically deuterated derivatives. Details of the method are to be described elsewhere.† It should be mentioned here, however, that in all our spectra only two bands are found which can reasonably be assigned to isotopic impurity (Table XII). Both of these are in the infra-red, and both are weak. From this we conclude that our exchange was very nearly as complete as the purity of our heavy water (99.6+ percent) would allow.

* Chemical Foundation Fellow, 1938–1942.

¹ W. W. Coblentz, *Investigations of Infra-Red Spectra* (Carnegie Institution of Washington, Washington, D. C., 1905) pp. 99, 143, 278.

² R. Manzoni-Ansidei and M. Rolla, *Atti accad. Lincei* **27**, 410 (1938).

³ S. Venkateswaran, *Ind. J. Phys.* **5**, 145 (1930).

⁴ G. B. Bonino, R. Manzoni-Ansidei, and P. Pratesi, *Zeits. f. physik. Chemie* **B22**, 21 (1933).

⁵ A. Stern and K. Thalmayer, *Zeits. f. physik. Chemie* **B31**, 403 (1936).

⁶ A. W. Reitz, *Zeits. f. physik. Chemie* **B33**, 179 (1936).

⁷ G. B. Bonino and R. Manzoni-Ansidei, *Ricerca Scient.* **7** (1), No. 11–12, 2 pp. (1936). *Or: Atti accad. Lincei* **25**, 489 (1937).

⁸ A. W. Reitz, *Zeits. f. physik. Chemie* **B38**, 275 (1938).

⁹ R. Manzoni-Ansidei, *Ricerca Scient.* **10**, 328 (1939).

¹⁰ G. B. Bonino and R. Manzoni-Ansidei, *Ricerca Scient.* **7** (2), No. 3–4 (1936). *Or: Atti accad. Lincei* **25**, 494 (1937).

¹¹ O. Redlich and W. Stricks, *Monats.* **68**, 47 (1936).

¹² M. Harada and T. Titani, *Bull. Chem. Soc. Jap.* **11**, 465–74 (1936); M. Koizumi and T. Titani, *ibid.*, **12**, 107–8 (1937); *ibid.*, **13**, 85–94 (1938).

† To appear shortly in *J. Am. Chem. Soc.*

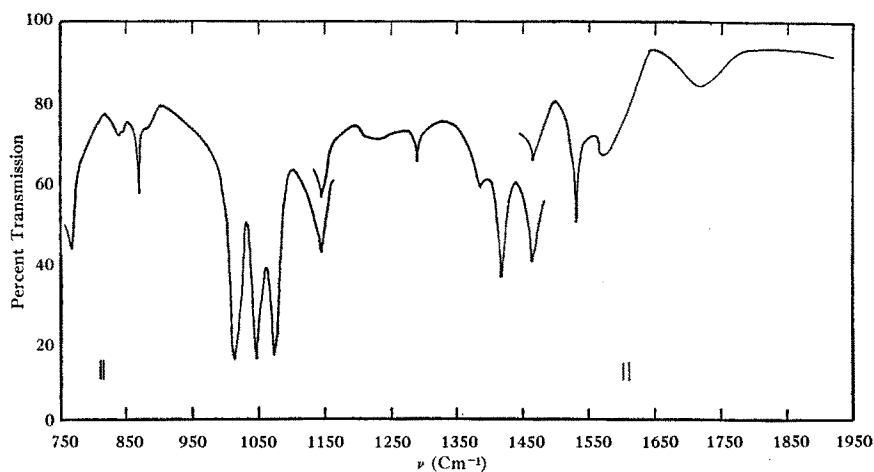


FIG. 1. Infra-red transmission curve for pyrrole. Cell thickness=0.020 mm.

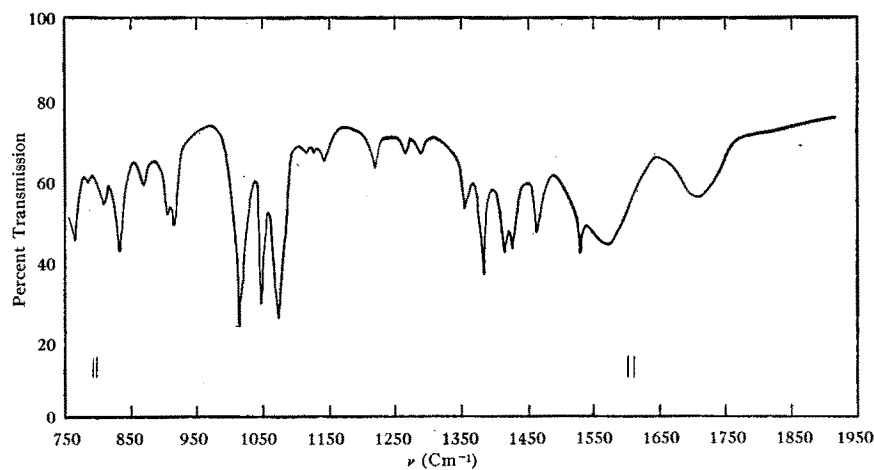


FIG. 2. Infra-red transmission curve for pyrrole-*N*- d . Cell thickness=0.020 mm.

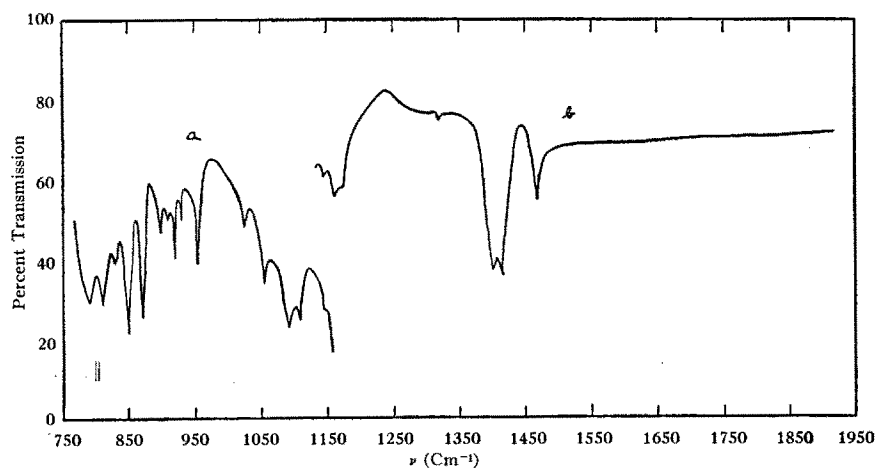


FIG. 3. Infra-red transmission curve for *sym*-pyrrole- d_4 . Cell thickness: *a*—0.045 mm. *b*—0.020 mm.

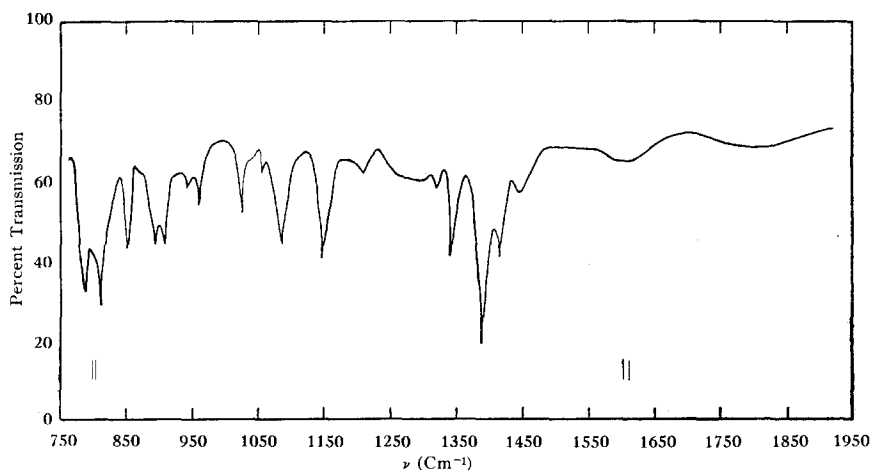


FIG. 4. Infra-red transmission curve for pyrrole- d_5 . Cell thickness = 0.028 mm.

The chief difficulty encountered in obtaining the Raman spectrum of pyrrole is the removal of the last traces of fluorescent impurities. To accomplish this removal the pyrrole was distilled four times and then sealed in the Raman tube, the entire series of operations being carried out in vacuum. After exposures totalling as much as 70 hours, samples were still free from fluorescence.

Spectroscopic Procedures

The Raman spectra were photographed with Hg 4358Å excitation. To isolate this frequency we used a filter of saturated aqueous NaNO_2 of sufficient thickness to remove Hg 4047Å almost completely. For a few exposures Rhodamine 5 GDN Extra was also used.¹³ The removal of background by this filter was offset by the somewhat longer exposure times which its use necessitated. The light source consisted of six General Electric H-2 type mercury arcs. These lamps are not particularly intense, but they have excellent background characteristics and are easily operated. The spectrograph is a plane grating instrument with an extremely fast camera, which was usually operated at a stop of $f: 3.8$. The grating, ruled by Professor R. W. Wood of the physics department, is of the echelette type. Its ruled surface is 4×6 inches, it has a total of 90,000 lines, and in the blue-green region it throws some 80 percent of the reflected light into one of the first orders. The

dispersion in the blue-green is 55Å/mm. Details of the construction of this instrument, as well as of the illuminator and filter cell, will be published elsewhere. The plates were Eastman Super Panchro Press, which are very fast but coarse-grained. For this reason a fine-grain developer was used (Eastman DK-20). Exposures varied from 1 to 24 hours, depending on the filters. The plates were enlarged 20 times, and the frequencies were measured from these enlargements by linear interpolation between standard lines of the iron arc with the help of a correcting curve. Sharp lines are probably accurate to $\pm 1 \text{ cm}^{-1}$, diffuse ones to $\pm 3 \text{ cm}^{-1}$.

The infra-red spectra were obtained in the liquid state in the range 750–1900 cm^{-1} . This work was done at the Stamford laboratories of the American Cyanamid Company through the kindness of Dr. R. Bowling Barnes, Director of the Physics Division, and Dr. Van Zandt Williams. The spectrometer is an automatic recording instrument which uses two rocksalt prisms in a Littrow mount.** The cells containing the liquid were made of rocksalt plates spaced at the proper distance by metal washers. The cell thicknesses were 0.020, 0.028, and 0.045 mm. The spectral slit widths varied from about 8 cm^{-1} at 1600 cm^{-1} down to 5 cm^{-1} at 800 cm^{-1} . Cell thicknesses and slit widths employed in obtaining the various curves are indicated on Figs. 1–4. The accuracy of the transmission

¹³ J. T. Edsall and E. B. Wilson, Jr., *J. Chem. Phys.* **6**, 125 (1938).

** A diagrammatic sketch of the instrument will be found in *Rev. Sci. Instr.* **13**, 50 (1942).

TABLE I. Raman spectra of the four pyrroles.

Pyrrole		Pyrrole-N-d		Symmetrical pyrrole-d ₄		Pyrrole-d ₅	
$\Delta\nu(\text{cm}^{-1})$	<i>I</i>	$\Delta\nu(\text{cm}^{-1})$	<i>I</i>	$\Delta\nu(\text{cm}^{-1})$	<i>I</i>	$\Delta\nu(\text{cm}^{-1})$	<i>I</i>
545-585	0 <i>b</i>	420-475	0 <i>b</i>	514	1-	425-475	1 <i>b</i>
(618)	0	606	3 <i>p</i>	560	6 <i>b</i>	516	1
647	3	708	3	692	4 <i>p</i>	565	4
711	3	(780)	0	730	2	693	3 <i>p</i>
837	2	831	3 <i>p</i>	769	1	728	2 <i>p</i>
866	1	869	2	848	4 <i>p</i>	766	1
880	$\frac{1}{2}$	911	2	917	4 <i>p</i>	808	1
1015	$\frac{1}{2}$	1010	1	953	1	892	5 <i>p</i>
1045	1	1074	5 <i>p</i>	1094	10 <i>p</i>	909	5 <i>p</i>
1076	3	1135	10 <i>p</i>	1319	7 <i>p</i>	1084	10 <i>p</i>
1144	10	1210	0	1401	9 <i>p</i>	1115-1170	3 <i>b</i>
1237	$\frac{1}{2}$	1237	$\frac{1}{2}$	1463	1	(1211)	0
1379	9 <i>b</i>	1320-80	3 <i>b</i>	2309	7 <i>p</i>	1317	5 <i>p</i>
1468	5	1384	9 <i>p</i>	2358	7 <i>p</i>	1389	8 <i>p</i>
(1484)	0	1465	6 <i>p</i>	3365-3455	3 <i>b</i>	(1413)	$\frac{1}{2}$
1528	$\frac{1}{2}$	2490-2560	5 <i>b</i>	—	—	1455	$\frac{1}{2}$
3100	4	(2709)	0	—	—	2309	8
3111	4	3104	8 <i>p</i>	—	—	2350	6 <i>p</i>
3133	9	3131	10 <i>p</i>	—	—	2368	6 <i>p</i>
3345-3460	4 <i>b</i>	—	—	—	—	2505-2560	6 <i>b</i>
		—	—			2679	$\frac{1}{2}$

() Observed on only one plate, but believed real.

b Broad.*p* Estimated to be polarized.

TABLE II. Raman spectrum of pyrrole: comparison with earlier work.

V. (1930) ^a	<i>I</i>	S. T. (1936) ^b	<i>I</i>	B. M.-A. (1936) ^c	<i>I</i>	$\Delta\nu$	R. (1938) ^d	<i>I</i>	Depol	L. M. (1942)	<i>I</i>
530	0	550	0	—	—	556	0	<i>dp.</i>	—	545-585	0 <i>b</i>
—	—	—	—	574	0	—	—	—	—	—	—
628	0	—	—	—	—	—	—	—	—	(618)	0
—	—	646	2 <i>d</i>	649	1	646	2	0.92	—	647	3
704	1	711	2 <i>d</i>	708	2	708	4	.94	—	711	3
843	0	840	1	835	$\frac{3}{2}$	835	3	.89	—	837	2
—	—	873	1	866	2	865	3	.92	—	866	1
—	—	—	—	—	—	—	—	—	—	880	$\frac{1}{2}$
1003	1	1000	0	1001	0	—	—	—	—	1015	$\frac{1}{2}$
—	—	1051	2	1046	$\frac{3}{2}$	1048	4	<i>dp.</i>	—	1045	1
—	—	—	—	1084	$\frac{3}{2}f?$	1072	1	<i>p.</i>	—	1076	3
—	—	1091	2	—	—	—	—	—	—	—	—
1144	8	1145	10	1142	10	1144	12	.18	—	1144	10
1202	0	—	—	1204	?	—	—	—	—	—	—
—	—	1233	0	1235	0	1235	1	.33	—	1237	$\frac{1}{2}$
—	—	1313	0	—	—	—	—	—	—	—	—
1384	4 <i>b</i>	1382	6	1380	6	1379	8 <i>b</i>	.36	—	1379	9 <i>b</i>
—	—	1416	0	1414	$\frac{1}{2}f?$	—	—	—	—	—	—
1470	3	1465	5	1465	5	1469	6	.22	—	1468	5
—	—	—	—	—	—	—	—	—	—	(1484)	0
—	—	1524	1	—	—	—	—	—	—	1528	$\frac{1}{2}$
—	—	1558	1	—	—	1562	1?	—	—	—	—
—	—	1593	0	—	—	—	—	—	—	—	—
—	—	1631	0	—	—	—	—	—	—	—	—
—	—	2676	0	—	—	—	—	—	—	—	—
—	—	2777	1	2786	0Hg?	—	—	—	—	—	—
—	—	2880	0	—	—	—	—	—	—	—	—
—	—	2926	1	—	—	2917	0	<i>p.</i>	—	—	—
3057	0	3056	1	3062	$\frac{1}{2}$ Hg?	3045	1?	— (Hg)	—	—	—
—	—	—	—	—	—	—	—	—	—	3100	4
—	—	3108	3	3107	3	3108	8	<i>p</i> (Hg)	—	3111	4
3139	6	3134	5	3138	5	3138	7 <i>b</i>	.44(Hg)	—	3133	9
3308	0 <i>b</i>	—	—	—	—	—	—	—	—	—	—
—	—	3388	2 <i>d</i>	3390	3 dif.	3383	3 <i>b</i>	.49(Hg)	—	3345-3460	4 <i>b</i>

() Found on only one plate, but believed real. ^a Reference 3. ^b Reference 5. ^c Reference 7. ^d Reference 8.

TABLE III. Raman spectrum of pyrrole-*N-d*: comparison with earlier work.

R. S. (1936) ^a $\Delta\nu$	<i>I</i>	B. M.-A. (1936) ^b $\Delta\nu$	<i>I</i>	L. M. (1942) $\Delta\nu$	<i>I</i>
291	0	—	—	—	—
—	—	456	0	420–475	0b
537?	0	—	—	—	—
—	—	572	0	—	—
608	2	608	$\frac{3}{2}$	606	3
—	—	652	0	—	—
708	2	710	2	708	3
—	—	—	—	(780)	0
832	2	835	1	831	3
—	—	867	1	869	2
—	—	912	2	911	2
—	—	1012	$\frac{1}{2}$	1010	1
—	—	1046	$\frac{1}{2}$	—	—
1072	3b	1080	$\frac{1}{2}$	1074	5
—	—	1104	00	—	—
1136	10	1136	10	1135	10
1147	1	—	—	—	—
—	—	—	—	1210	0
—	—	1236	$\frac{1}{2}$	1237	$\frac{1}{2}$
—	—	—	—	1320–80	3b
1386	9	1383	7	1384	9
—	—	1414	0-f?	—	—
1465.5	4	1465	5	1465	6
2357	0	—	—	—	—
—	—	2536	3d	2490–2560	5b
—	—	—	—	(2709)	0
—	—	2788	$\frac{1}{2}$	—	—
—	—	3023	0?	—	—
—	—	3051	0-Hg	—	—
3104.5	3	3109	3	3104	8
3135	5	3138	5	3131	10

() Found on only one plate.

^a Reference 11.^b Reference 10.

minima varies from about 5 cm⁻¹ in the 1600-cm⁻¹ region to 2 cm⁻¹ in the 800-cm⁻¹ region. The upper limit of 1900 cm⁻¹ to the spectral range studied was dictated by considerations of time. The only fundamental frequencies beyond this region are the "hydrogen" stretching frequencies, which are Raman active, and concerning whose interpretation there is no serious question.

EXPERIMENTAL RESULTS

Raman Spectra

The results of the Raman studies on the four pyrroles are given in Table I. The intensities listed there have been visually estimated on an arbitrary scale of 10. Those lines which seemed to be polarized, judging from their sharp appearance on the plates, are labelled *p*.¹⁴ In

¹⁴ This method of estimating polarization is not entirely trustworthy, as has been pointed out by J. R. Nielsen and N. E. Ward (J. Chem. Phys. 10, 87 (1942)). Our assignments contravene our estimates of depolarization in 5 instances.

TABLE IV. Infra-red spectra of the four pyrroles.

Pyrrole cm ⁻¹	<i>I</i>	Pyrrole- <i>N-d</i> cm ⁻¹	<i>I</i>	sym-pyrrole- <i>d</i> ₄ cm ⁻¹	<i>I</i>	Pyrrole- <i>d</i> ₃ cm ⁻¹	<i>I</i>
768	<i>s</i>	766	<i>s</i>	793	<i>s</i>	789	<i>vs</i>
839	<i>w</i>	783	<i>vw</i>	812	<i>s</i>	813	<i>vs</i>
844	<i>vw</i>	786	<i>vw</i>	830	<i>w</i>	852	<i>s</i>
869	<i>m</i>	808	<i>m</i>	849	<i>vs</i>	893	<i>s</i>
884	<i>w</i>	835	<i>s</i>	872	<i>vs</i>	910	<i>s</i>
1015	<i>vs</i>	870	<i>m</i>	899	<i>m</i>	943	<i>w</i>
1047	<i>vs</i>	905	<i>m</i>	910	<i>w</i>	961	<i>m</i>
1076	<i>vs</i>	915	<i>s</i>	920	<i>s</i>	1025	<i>s</i>
1146	<i>s</i>	1015	<i>vs</i>	931	<i>m</i>	1039	<i>vw</i>
1289	<i>m</i>	1026	<i>w</i>	956	<i>s</i>	1058	<i>w</i>
1384	<i>m</i>	1048	<i>vs</i>	1027	<i>m</i>	1085	<i>s</i>
1418	<i>s</i>	1074	<i>vs</i>	1058	<i>m</i>	1131	<i>vw</i>
1466	<i>s</i>	1116	<i>vw</i>	1093	<i>s</i>	1147	<i>s</i>
1531	<i>s</i>	1126	<i>vw</i>	1111	<i>m</i>	1210	<i>m</i>
—	—	1143	<i>w</i>	1147	<i>vw</i>	1318	<i>w</i>
—	—	1220	<i>m</i>	1163	<i>s</i>	1341	<i>s</i>
—	—	1265	<i>w</i>	1178	<i>vw</i>	1389	<i>vs</i>
—	—	1290	<i>w</i>	1318	<i>vw</i>	1415	<i>s</i>
—	—	1354	<i>m</i>	1401	<i>vs</i>	1442	<i>w</i>
—	—	1384	<i>s</i>	1415	<i>vs</i>	—	—
—	—	1418	<i>s</i>	1468	<i>s</i>	—	—
—	—	1428	<i>s</i>	—	—	—	—
—	—	1464	<i>s</i>	—	—	—	—
—	—	1532	<i>m</i>	—	—	—	—

vs Very strong. *s* Strong. *m* Medium. *w* Weak. *vw* Very weak.

TABLE V. Infra-red spectrum of pyrrole: comparison with earlier work.

C. (1905) ^a cm ⁻¹	<i>I</i>	M.-A. and R. (1938) ^b cm ⁻¹	<i>I</i>	L. M. (1942) cm ⁻¹	<i>I</i>
—	—	647	<i>m</i>	—	—
—	—	728	<i>vs</i>	768	<i>s</i>
781	<i>vw</i>	—	—	—	—
—	—	826	<i>w</i>	839	<i>w</i>
—	—	—	—	844	<i>vw</i>
873	<i>s</i>	864	<i>w</i>	869	<i>m</i>
—	—	—	—	884	<i>w</i>
972	<i>vw</i>	—	—	—	—
1005	<i>vs</i>	—	—	1015	<i>vs</i>
—	—	1026	<i>s</i>	—	—
1052	<i>w</i>	—	—	1047	<i>vs</i>
1075	<i>vs</i>	1069	<i>s</i>	1076	<i>vs</i>
1130	<i>s</i>	1149	<i>w</i>	1146	<i>s</i>
1202	<i>w</i>	—	—	—	—
1273	<i>w</i>	—	—	—	—
—	—	—	—	1289	<i>m</i>
—	—	—	—	1384	<i>m</i>
1418	<i>vs</i>	1418	<i>vs</i>	1418	<i>s</i>
—	—	—	—	1466	<i>s</i>
1540	<i>vs</i>	—	—	1531	<i>s</i>
1600	<i>vw</i>	—	—	—	—
1710	<i>m</i>	—	—	—	—
2100	<i>w</i>	—	—	—	—
2260	<i>w</i>	—	—	—	—
2530	<i>s</i>	—	—	—	—
2800	<i>vw</i>	—	—	—	—
3100	<i>vw</i>	—	—	—	—
3390	<i>vs</i>	—	—	—	—

vs Very strong. *s* Strong. *m* Medium. *w* Weak. *vw* Very weak. ^a Reference 1. ^b Reference 2.

TABLE VI. Selection rules for pyrrole: C_{2v} symmetry.

Class	Essential symmetry elements		Ring	Normal vibrations		Total	Selection rules	
	$C_2(z)$	$\sigma_v(yz)$		Stretching	Bending		Ram.	I. R.
A_1	+	+	T_z	3	2	9	$+p$	+
B_1	—	+	T_x, R_y	2	3	8	$+dp$	+
A_2	+	—	R_z	0	2	3	$+dp$	—
B_2	—	—	$T_y R_z$	0	3	4	$+dp$	+

TABLE VII. Selection rules for D_{3h} symmetry.*

Class	Essential symmetry elements			T and R	Normal vibrations			Selection rules		Vibrations become in C_{2v}	
	$C_3(z)$	$C_2(x)$	$\sigma_h(yz)$		C	H	Total	Ram.	I. R.	Class	No.
A'_1	+	+	+		1	1	2	+	—	A_1	2
A'_2	+	—	+	R_y	0	1	1	—	—	B_1	1
A''_1	+	+	—		0	0	0	—	—	A_2	0
A''_2	+	—	—	T_y	0	1	1	—	+	B_2	1
E'_1	$e \pm$	\pm	+	T_{xz}	1	2	3	—	+	A_1	7
E'_2	$e \pm 2$	\pm	+		2	2	4	+	—	B_1	7
E''_1	$e \pm$	\pm	—	R_{xz}	0	1	1	+	—	A_2	3
E''_2	$e \pm 2$	\pm	—		1	1	2	—	—	B_2	3

* For the derivation of this table see, e.g., Tisza, Zeits. f. Physik **82**, 48 (1933), or Rosenthal and Murphy, Rev. Mod. Phys. **8**, 317 (1936).

TABLE VIII. Moments of inertia for the pyrroles: C_{2v} symmetry. ($\times 10^{-40}$ g cm²).

	Pyrrole	Pyrrole- $N-d$	sym-Pyrrole- d_4	Pyrrole- d_5
I_x	89	97	102	109
I_y	186	194	221	228
I_z	97	97	119	119

Table II our results for pyrrole are compared with those of previous investigators. It will be seen that there is general agreement except for a number of weak frequencies reported by Stern and Thalmayer. There seems to be some question as to the purity of the sample used by these investigators, however,^{7,9} and we feel that this is a fair way of explaining these weak lines. Owing to the high resolving power of our instrument, two lines (866 and 3108 cm⁻¹) have each been resolved into two components in our spectra. Inasmuch as our work agrees generally with earlier results, we feel that our frequencies for pyrrole represent fairly its Raman spectrum. In Table II we have also included the results of Reitz' depolarization measurement.⁸

Two previous studies have been made of pyrrole- $N-d$.^{10,11} These results are compared with ours in Table III. The agreement is reasonably satisfactory. Bonino and Manzoni-Ansidei report finding more lines than were found by either

Redlich and Stricks or by ourselves. Frequencies which they alone report are 572, 652, 1046, 1104, 1414, 2788, 3023, and 3051 cm⁻¹. We shall see later that two of these, 1046 and 1414, are unquestionably fundamental frequencies in pyrrole- $N-d$; we have found them in the infra-red. Bonino and Manzoni-Ansidei themselves suggest that 2788 and 3051 cm⁻¹ may be caused by weak lines of their Hg arcs. This is supported by the facts that these same frequencies appear in their spectrum of pyrrole, and that we do not find them on our plates. 3023 is presumably an overtone or combination tone. 1104 is reported as exceedingly weak; we find no trace of it. This leaves 572 and 652 to be explained. It is to be noted that both of these frequencies appear in the Raman spectrum of pyrrole reported by Bonino and Manzoni-Ansidei. 572, however, is of low intensity in pyrrole, and it is surprising that Bonino and Manzoni-Ansidei should have observed it in pyrrole- $N-d$ if it really is caused by isotopic impurity. On the other hand, this is the N—H out-of-plane bending frequency in pyrrole (Table XI); hence it is a frequency which should be very sensitive to any N—H impurity in a sample of pyrrole- $N-d$. The 652 frequency is somewhat stronger in pyrrole, and can probably show up weakly in the Raman spectrum of pyrrole- $N-d$ contaminated with ordinary pyrrole.

TABLE IX. Frequency product ratios (τ 's): C_{2v} symmetry.

Class		Pyrrole Pyrrole- d_5	Pyrrole Pyrrole- d_4	Pyrrole Pyrrole- $N-d$	Pyrrole- $N-d$ Pyrrole- d_5	Pyrrole- $N-d$ Pyrrole- d_4	Pyrrole- d_4 Pyrrole- d_5
A_1	Calc.	5.46	3.89	1.40	3.89	2.77	1.40
	Obs.	5.21	3.75	1.37	3.81	2.74	1.39
B_1	Calc.	4.93	3.56	1.38	3.58	2.59	1.38
	Obs.	4.60	3.36	1.35	3.41	2.49	1.37
A_2	Calc.	1.80	1.80	1.00	1.80	1.80	1.00
	Obs.	1.80	1.80	1.00	1.80	1.80	1.00
B_2	Calc.	2.43	1.82	1.35	1.83	1.35	1.36
	Obs.	—	—	1.29	—	—	—

TABLE X. Infra-red and Raman spectra of the four pyrroles.

Pyrrole		Pyrrole- $N-d$		<i>sym</i> -pyrrole- d_4		Pyrrole- d_5	
Raman	Infra-red	Raman	Infra-red	Raman	Infra-red	Raman	Infra-red
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I
565	0b	450	0b	514	1	450	1b
(618)	0	606	3	560	6b	516	1
647	3	708	3	692	4	565	4
711	3	—	—	730	2	693	3
—	—	(780)	0	766	s	728	2
837	2	—	—	783	vw	766	1
—	—	—	—	786	vw	—	—
—	—	—	—	808	m	793	s
866	1	831	3	—	—	812	s
880	$\frac{1}{2}$	869	2	835	s	830	w
1015	$\frac{1}{2}$	884	2	870	m	849	vs
1045	1	911	2	905	m	872	vs
1076	3	—	—	915	s	899	m
1144	10	1010	1	1015	vs	910	w
1237	$\frac{1}{2}$	—	—	1026	w	920	s
—	—	—	—	1048	vs	931	m
—	—	1074	5	1074	vs	956	s
1379	9b	—	—	1116	vw	1027	m
—	—	—	—	1126	vw	1058	m
1468	5	1135	10	—	—	1093	s
(1484)	0	—	—	1094	10	1084	10
1528	$\frac{1}{2}$	1210	0	—	—	1111	m
—	—	—	—	—	—	1147	vw
—	—	1237	$\frac{1}{2}$	—	—	1163	s
—	—	—	—	—	—	(1211)	0
—	—	—	—	1265	w	1317	5
—	—	—	—	1290	w	—	—
—	—	1350	3b	1319	7	1318	vw
—	—	1384	9	1401	9	1401	vs
—	—	—	—	—	—	1389	8
—	—	—	—	1463	1	1415	vs
—	—	—	—	—	—	(1413)	$\frac{1}{2}$
—	—	1418	s	—	—	1455	$\frac{1}{2}$
—	—	1428	s	—	—	—	—
—	—	1464	s	—	—	—	—
—	—	1532	m	—	—	—	—
3100	4	2525	5b	2309	7	2309	8
3111	4	(2709)	0	2358	7	2350	6
—	—	—	—	—	—	2368	6
3133	9	3104	8	3410	3b	2535	6b
3400	4b	3131	10	—	—	2679	$\frac{1}{2}$

() Observed on only one plate, but believed real.

Redlich and Stricks report a line at 1147 cm^{-1} ; this is probably the corresponding strong line of pyrrole. We also found no trace of the frequencies reported by them at 291 and 537 cm^{-1} . These same authors seem to have made an error, perhaps typographical, in the N-D stretching frequency. They report it at 2357 cm^{-1} , whereas it actually occurs in the neighborhood of 2530 cm^{-1} . Apart from these exceptions, there is general agreement between the three spectra.

The assignment of lines to the proper exciting frequencies in *sym*-pyrrole- d_4 was straightforward and offered no problem. In pyrrole- d_5 , the 808-cm^{-1} Raman frequency excited by Hg 4358A coincides with the 909 frequency excited by Hg 4339A. The intensity of this line, however, which is greater than that of the 909 Raman line caused by Hg 4348A, leaves no doubt that 808 cm^{-1} is real. The 1413 frequency, although measured on only one plate, can be seen on several others.

It occurs as a wing on the edge of the strong 1389-cm^{-1} band, and any overexposure tends to merge the two.

Infra-Red Spectra

The infra-red transmission curves for the four pyrroles are shown in Figs. 1–4. The frequencies of the transmission minima have been tabulated in Table IV with a qualitative estimate of their intensities.

The infra-red absorption spectrum of pyrrole has been obtained previously by Coblenz¹ and by Manzoni-Ansidei and Rolla.² Both of these studies were made on the liquid, although Manzoni-Ansidei and Rolla do not explicitly say so. The latter authors give no cell sizes, but since they compare their work with that of Coblenz without comment on the state of aggregation, we must presume that their studies, like his and like ours, were made on the liquid. These results are compared in Table V. The general agreement of the spectra in regions where they overlap is not bad. Most noteworthy are the facts that the $1015\text{--}1047\text{ cm}^{-1}$ doublet is reported as unresolved by Manzoni-Ansidei and Rolla at 1026 cm^{-1} , and that the strong frequency found by us at 768 cm^{-1} must be considered as unreported by Manzoni-Ansidei and Rolla or else identified with the very strong absorption reported by them at 728 cm^{-1} . The infra-red spectra of the other three pyrroles have not been obtained previously.

DISCUSSION OF RESULTS

As a working hypothesis we will assume that the pyrrole molecule has C_{2v} symmetry. This is in accordance with chemical evidence for the structure of pyrrole, and with the results of the electron diffraction studies.¹⁵ The allocation of the 24 vibrational degrees of freedom to the various C_{2v} symmetry classes, and the selection rules for these classes, are shown in Table VI. The 2-fold axis through the nitrogen atom is picked as the z axis. The y axis is chosen perpendicular to the plane of the molecule and intersecting the z axis at the center of gravity. The x axis is then picked perpendicular to the

y and z axes and passing through their intersection. It will later prove convenient to have also the allocation of frequencies for a planar 10-atom molecule of D_{6h} symmetry. This is given in Table VII.

The usefulness of the spectra of deuterium derivatives for purposes of vibrational analysis is greatly enhanced by application of the Teller product rule. This rule has been discussed in detail elsewhere.¹⁶ By its use one can calculate, independently of spectroscopic observation, the ratio (denoted by τ) between the product of a certain set of frequencies in one isotopic form of a molecule, and the product of the same set in another isotopic form. By a "set" one means a collection of frequencies whose modes of vibration have a common symmetry. If the two isotopic forms under consideration belong to the same symmetry group (as will be true in our case), the sets to which the product rule is applicable are simply the symmetry classes of that group. In order to calculate these theoretical τ 's, a knowledge of the moments of inertia of the several pyrroles is essential. These moments have been calculated from the geometrical data given by Schomaker and Pauling,¹⁵ with the additional assumptions that the C–H distance is 1.09Å, the N–H distance 1.02Å, and that the C–H bond line bisects the ring angle when extended into the ring. The moments are given in Table VIII. The theoretical τ 's for the various symmetry classes and for the various pairs of deuterium derivatives are given in Table IX.

We now proceed to the assignment of the various frequencies to their symmetry classes. For convenience in discussing the spectroscopic data, the infra-red and Raman results are brought together in Table X. Table V will summarize our assignments, and will be of aid in tracing a given frequency through the four pyrroles.

1. Class A_1

The C_{2v} model requires nine totally symmetrical vibrations. Of these, two are C–H stretching frequencies and one the N–H stretching frequency, which we can assign without

¹⁵ V. Schomaker and L. Pauling, J. Am. Chem. Soc. **61**, 1776 (1939). This work, of course, leaves open the question of the positions of the hydrogen atoms.

¹⁶ Angus, Bailey, Hale, Ingold, Leckie, Raisin, Thompson, and Wilson state the product rule without proof (J. Chem. Soc., p. 978 (1936)). It was first published with proof by O. Redlich, who found it independently (Zeits. f. physik. Chemie **B28**, 371 (1935)).

TABLE XI. Frequency assignments: C_{2v} symmetry.

Class	No.	Pyrrole	Pyrrole- <i>N-d</i>	<i>sym</i> -pyrrole- <i>d</i> ₄	Pyrrole- <i>d</i> ₅
A_1	1	711	708	692	693
	2	1076	1074	812	813
	3	1144	1135	1094	1084
	4	1237	1237	919	909
	5	1384*	1384	1319	1317
	6	1467	1465	1401	1389
	7	3100	3104	2309	2309
	8	3133	3131	2358	2350
	9	3400	2525	3410	2535
B_1	10	647	606	560	565
	11	1015	1012	793	789
	12	1046	1048	848	808
	13	(1146)	915	1163	892
	14	1418	1418	1415	1415
	15	1530	1532	1465	1455
	16	3111	(3104)	(2309)	(2309)
	17	(3133)	(3131)	(2358)	2368
A_2	18	[510]	[510]	[440]	[440]
	19	(711)	(708)	514	516
	20	868	869	769	766
B_2	21	565	450	(560)	450
	22	768	766	[610]	[590]
	23	838	833	730	728
	24	(1046)	1026	872	852

() Used twice.

[] Calculated with the help of the product rule.

* The infra-red frequency value. The Raman band is diffuse.

hesitation to the 3100 and the 3400 cm^{-1} regions, respectively. The shifts in the deuterium derivatives are completely in accordance with this assignment.¹⁷ We are then left with six vibrations to be located in the region below 2000 cm^{-1} . Reitz has found five polarized lines in this region (Table II), and these five lines can be assigned bodily to the A_1 class. The sixth frequency then remains to be located. One would expect to find this well below 1000 cm^{-1} , since there must be one totally symmetric ring bending vibration, and since none of the five polarized lines lies below 1000 cm^{-1} . As a matter of fact, analogy with other ring compounds whose spectra have been analyzed leads one to expect this frequency at about 600–700 cm^{-1} . We select for it the frequency 711 cm^{-1} . 711 is found to be completely depolarized, as are all the other lines in this region, but this may be caused by the fact that the 711 line is a composite of a strong non-totally symmetrical frequency and a consider-

¹⁷ It may be worth mentioning that the N–H frequencies appear as very broad bands in the Raman spectra. This can doubtless be attributed to hydrogen bonding.

ably less intense symmetrical frequency. This interpretation is borne out by the broad nature of the 711 line and by the frequency changes in *sym*-pyrrole-*d*₄ and pyrrole-*d*₅. A sharp line appears in both of these compounds at 692 cm^{-1} which can scarcely have any other analogue in pyrrole than 711 cm^{-1} . The interpretation is further substantiated by the Raman spectrum of furan,⁸ in which there appears only one polarized line of frequency less than 1000 cm^{-1} . This line, whose depolarization factor has the rather large value 0.63, occurs at 724, a value sufficiently close to 711 to enable us to call the two lines analogous. The other constituent of the 711 line of pyrrole will be discussed under the A_2 symmetry class.

All six of the low A_1 frequencies can be traced unambiguously through the four deuterium derivatives. The agreement of the observed product rule τ 's with the calculated τ 's (Table IX) is quite satisfactory in view of the usual small deviations that are expected because of anharmonicity.

The intensity changes produced by deuterium substitution are very marked, and the spectra would be exceedingly difficult to analyze without having both the Raman and infra-red data. The A_1 class is no exception to this. A case in point is the 1076 frequency. This appears with great intensity in both the Raman and infra-red spectra of pyrrole and pyrrole-*N-d*. The analogous frequency in *sym*-pyrrole-*d*₄ and pyrrole-*d*₅, 812 cm^{-1} , is, however, completely missing in the Raman effect. It is true that there is a frequency in the Raman spectrum of pyrrole-*d*₅ at 808 cm^{-1} , but this is better ascribed to a B_1 vibration. Another case is the totally symmetric "breathing" frequency (1145 cm^{-1} in pyrrole), which undergoes very marked intensity changes in the infra-red. Inasmuch as there is no trouble whatever in tracing this very intense and highly polarized line in the Raman effect, we know exactly where to look for it in the infra-red. A rather broad band of marked intensity is indeed observed in the infra-red spectrum of pyrrole. We prefer, however, not to identify this band with the totally symmetric "breathing" frequency. In the first place, the analogous band is *completely* missing from the infra-red spectrum of pyrrole-*N-d*. Secondly, it should be noticed

that for a molecule of D_{5h} symmetry, this vibration is forbidden to appear in the infra-red (Table VII). Therefore one would expect that in a C_{2v} molecule which does not deviate too much from one of D_{5h} symmetry, the frequency will appear only weakly in the infra-red. We have, moreover, a satisfactory alternative assignment for this band in pyrrole which will be discussed later. The weak A_1 frequency at 1237 cm^{-1} is missing from the infra-red spectra of pyrrole and pyrrole- $N-d$, but the analogous frequencies in the other two compounds (919 and 909 cm^{-1}) are strong in both the Raman effect and the infra-red. The quantitative frequency changes, however, leave little doubt that these frequencies are to be assigned to the same modes of vibration. The remaining totally symmetrical frequencies occur with more or less regular intensity changes.

2. Class B_1

The location of the B_1 frequencies can be facilitated if one notes that all but one of the B_1 frequencies of the C_{2v} molecule are derived from the E'_1 and E'_2 frequencies of the D_{5h} molecule by the release of the double degeneracy of the latter (Table VII). Those $E'_{1,2}$ frequencies which do not become B_1 frequencies go into class A_1 upon the release of the degeneracy. In consequence we might expect that the A_1 frequencies should to a certain extent be paired up with the B_1 frequencies, except for those two A_1 vibrations which correspond to the totally symmetrical vibrations of the D_{5h} molecule and for the single B_1 vibration which corresponds to the A'_2 vibration of D_{5h} . The latter is essentially one of hydrogen bending. All the B_1 ring frequencies should thus occur in the neighborhood of their A_1 counterparts. These A_1 frequencies are 711 , 1384 , and 1467 cm^{-1} in pyrrole (cf. Table XI). The frequencies nearby are 647 , 1418 , and 1530 cm^{-1} . These we assign to class B_1 . Of the five hydrogen vibrations in class B_1 , two are essentially C—H stretching, two C—H bending, and one N—H bending. The C—H stretching frequencies are to be assigned to the 3100-cm^{-1} region. By analogy with the A_1 bending frequencies, we assign the lines at 1015 and 1046 to C—H bending.

The N—H bending frequency is more difficult to locate. There are several general statements

which we may make, however, before starting a methodical search for it. First, if it is as high as $1500\text{--}1600\text{ cm}^{-1}$, it should shift to $1100\text{--}1200\text{ cm}^{-1}$ in the N—D substituted compounds. We then expect that this frequency will never interact with the C—H or C—D bending frequencies except in pyrrole- $N-d$, for in both *sym*-pyrrole- d_4 and pyrrole- d_5 the C—D bending frequencies are much too low. If on the other hand the N—H frequency is considerably lower, we might expect to find marked evidence of interaction with C—H bending vibrations in pyrrole, and with C—D bending vibrations in pyrrole- d_5 . We observe the following facts: (a) There are no Raman nor infra-red frequencies in the $1500\text{--}1600\text{-cm}^{-1}$ region whose frequency changes upon deuterium substitution are compatible with the mass change of two. (b) The difference in the $800\text{--}1000\text{-cm}^{-1}$ region between the spectra of pyrrole and pyrrole- $N-d$, and between *sym*-pyrrole- d_4 and pyrrole- d_5 is marked. These differences indicate strongly that some interaction is occurring. At first one might ascribe this interaction to members of the B_2 class, but we will show later that the N—H frequency in B_2 lies entirely outside of this region at 565 cm^{-1} . Since the B_1 class is the only other class containing an N—H bending frequency, we are virtually compelled to locate the N—D frequency in the $800\text{--}1000\text{-cm}^{-1}$ region. This puts the N—H frequency at about $1000\text{--}1200\text{ cm}^{-1}$. A search of the infra-red and Raman spectra in this region reveals only one significant change on passing from pyrrole to pyrrole- $N-d$. This is the absence, referred to earlier, of the 1146-cm^{-1} band in the infra-red spectrum of pyrrole- $N-d$. We therefore ascribe the 1146-cm^{-1} band in pyrrole to the N—H bending. The shift in the N—H frequency upon deuterium substitution should put it in the neighborhood of $850\text{--}900\text{ cm}^{-1}$. Actually there is observed a new Raman frequency and a new infra-red band in pyrrole- $N-d$ at 915 cm^{-1} . The unexpected appearance of a frequency in this neighborhood can scarcely be understood on any other basis. This assignment is substantiated by the spectra of pyrrole- d_4 and pyrrole- d_5 . In the latter compounds the N—H and N—D frequencies occur, respectively, at 1163 and 892 cm^{-1} .

As can be seen from Table IX, the product rule is reasonably well satisfied by these assignments. Corroboration of the assignments is also indicated by the remarkable frequency and intensity changes which occur in the 800–900 cm^{-1} region in going from *sym*-pyrrole- d_4 to pyrrole- d_5 . The 848 Raman line in the former compound changes markedly in frequency and intensity, dropping to 808 cm^{-1} in pyrrole- d_5 and becoming much less intense. The change can be readily understood if we attribute it to interaction between this C–D and the N–D bending frequencies. Such an interaction will cause the two frequencies to separate and their Raman intensities to mix. We thus can understand the remarkable drop from 848 to 808, the accompanying loss of intensity, and the great increase in the intensity of the N–D frequency at 892

cm^{-1} in the Raman effect. The only remaining comment on the B_1 frequencies is to remark the surprising constancy of the 1418 cm^{-1} ring vibration. The fact that this frequency shifts by only a few wave numbers in going from pyrrole to pyrrole- d_5 is presumably to be ascribed to the lack of appreciable participation of the hydrogen atoms in the mode of vibration.

3. Class A_2

It should in principle be easy to locate the A_2 frequencies, for these should show no change in going from pyrrole to pyrrole- N - d , and from *sym*-pyrrole- d_4 to pyrrole- d_5 . Moreover, they should be missing from the infra-red spectra. Unfortunately the infra-red measurements do not extend to sufficiently low frequencies to cover the region of all the A_2 vibrations. In addition we may note that in the case of benzene analogous frequencies appear with some intensity in the infra-red spectrum of the liquid, although they are missing in the spectrum of the vapor.¹⁸ Analogy with benzene leads us to assign the 711 Raman line to the A_2 class. This frequency shifts by the proper amount to 515 cm^{-1} in pyrrole- d_4 and pyrrole- d_5 . Another Raman line satisfying the A_2 criterion is 868 in pyrrole. This leaves one additional A_2 frequency, which we suppose is not Raman active. This is not surprising, inasmuch as ring distortion vibrations of this type are generally weak in the Raman effect. It is possible that the numerical value of this frequency will not be far from the analogous frequency in furan. An extremely weak Raman line is observed in the latter molecule at 500 cm^{-1} .^{6,8} If we assume that an A_2 frequency lies at 510 cm^{-1} in pyrrole, we can explain several overtones and combination tones which are otherwise hard to understand. This should shift to the neighborhood of 450 cm^{-1} in *sym*-pyrrole- d_4 and pyrrole- d_5 . One combination tone in the spectrum of the former can be explained by the assumption of a fundamental at 440 cm^{-1} . These values fit the product rule for class A_2 .

4. Class B_2

Of the B_2 frequencies, the easiest one to assign is the N–H out-of-plane bending vibra-

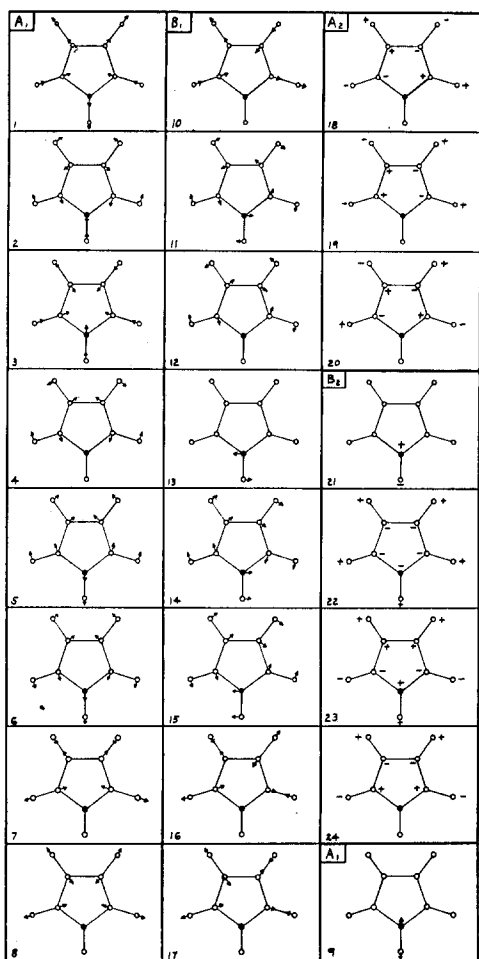


FIG. 5. Modes of vibration for pyrrole (schematic).

¹⁸ Bailey, Hale, Ingold, and Thompson, J. Chem. Soc., p. 931 (1936).

TABLE XII. Left-over frequencies and suggested assignments.

Pyrrole			Pyrrole- <i>N-d</i>			<i>sym</i> -pyrrole- <i>d</i> ₄			Pyrrole- <i>d</i> ₅		
Obs.	Calc.	Assign- ment	Obs.	Calc.	Assign- ment	Obs.	Calc.	Assign- ment	Obs.	Calc.	Assign- ment
618	616	$\nu_5 - \nu_{22}$	783	778	$\nu_5 - \nu_{10}$	830	—	—	943	939	$\nu_6 - \nu_{21}$
844	*		786	787	$\nu_4 - \nu_{21}$	899	901	$\nu_{14} - \nu_{19}$	961	966	$\nu_{19} + \nu_{21}$
882	883	$\nu_{15} - \nu_{10}$	808	812	$\nu_{14} - \nu_{10}$		905	$\nu_{15} - \nu_{10}$	1025	1032	$2\nu_{19}$
1289	1294	$2\nu_{10}$	905	900	$2\nu_{21}$	910	—	N-D impurity	1039	—	—
1484	1485	$\nu_{10} + \nu_{23}$	1116	1116	$\nu_{10} + \nu_{18}$	931	—	—	1058	—	—
			1126	*		955	954	$\nu_{18} + \nu_{19}$	1131	1130	$2\nu_{10}$
			1143	—	N-H impurity	1027	1028	$2\nu_{19}$	1147(b)	1130	$2\nu_{10}$
			1210	1212	$2\nu_{10}$	1058	—	—		1143	$\nu_1 + \nu_{21}$
			1220	1218	$\nu_{18} + \nu_{19}$	1111	1120	$2\nu_{10}$		1180	$2\nu_{22}$
			1265	1276	$\nu_{18} + \nu_{22}$	1147	—	—			
			1290	1283	$\nu_{21} + \nu_{23}$	1178	—	—			
				1350	$3\nu_{21}$				1210	1216	$\nu_{20} + \nu_{21}$
			1354	1365	$\nu_{13} + \nu_{21}$					1209	$\nu_1 + \nu_{19}$
				1425	$\nu_{13} + \nu_{18}$					1341	$3\nu_{21}$
			1428	1425	$\nu_{13} + \nu_{18}$					1442	—
			2709	2702	$\nu_4 + \nu_6$					2679	—

* Cannot be explained as binary combination tone.

tion. This frequency occurs as a fuzzy line at 565 cm^{-1} in the N—H compounds and at 450 cm^{-1} in the N—D compounds. The large shift marks it immediately.¹⁹ It is perhaps rather surprising that a hydrogen frequency should be so low. This low value is doubtless associated with the flatness of the potential curve for the bending. In the ammonia molecule the potential curve for the symmetrical bending vibration has two minima separated by a low maximum. In pyrrole, resonance between electronic structures involving a neutral and a positively charged nitrogen atom may wash out this maximum, leaving a flattened potential curve with a single minimum at the point where the N—H bond lies in the ring plane.

Of the remaining B_2 frequencies, one should be strongly active in the infra-red, namely, the one associated with the anti-translational mode of vibration (ν_{22} , Fig. 5). Our curves show a strong absorption at 768 cm^{-1} , which is a reasonable place for this vibration to appear. We find no evidence of a 768 frequency in the Raman effect, which is compatible with the fact that the corresponding D_{5h} frequency (A''_2) is forbidden. Unfortunately we cannot observe this frequency in the infra-red spectra of *sym*-pyrrole- d_4 and pyrrole- d_5 as it lies below 750 cm^{-1} . One of the two remaining B_2 frequencies may be assigned to the line at 838 cm^{-1} . A reasonable shift to 730

cm^{-1} is observed for this in the heavier compounds. The other B_2 frequency has been tentatively located by the difficulty of otherwise assigning a band shoulder at 1026 cm^{-1} in pyrrole-*N-d*. We have not been able to get a satisfactory explanation of this frequency as a combination tone, and we tentatively assign it to B_2 . A reasonable shift for this frequency in the deuterium derivatives would place it at about 850 cm^{-1} and indeed two very similar bands, one at 872 cm^{-1} in pyrrole- d_4 and the other at 852 in pyrrole- d_5 , have been found. By means of the product rule we can place this frequency at about 1045 cm^{-1} in pyrrole, where it coincides with a B_1 frequency. By the same procedure we can calculate a value of 610 and of 590 cm^{-1} for the unobserved ν_{22} frequency in pyrrole- d_4 and pyrrole- d_5 .

A summary of the foregoing assignments is given in Table XI. In Fig. 5 we have represented schematically the modes of vibration for the C_{2v} model of pyrrole. These are determined to some extent by symmetry and by the orthogonality relationships.²⁰ In addition, the assumption of a valence-force potential system for pyrrole enables one to make a rough guess at the form of the vibrations. It is to be emphasized that the modes pictured in Fig. 5 are simply approximations which can be helpful when one is estimating frequency shifts, spectroscopic intensities, and the like.

¹⁹ In pyrrole- d_4 the 560- cm^{-1} N—H frequency overlies the 565- cm^{-1} B_1 frequency. This is clearly indicated by the fuzziness of the line; in pyrrole- d_5 , the B_1 frequency at 565 cm^{-1} is sharp.

²⁰ E. Teller, *Hand- und Jahrbuch der chemischen Physik* 9 (2), pp. 95 ff.

5. Left-Over Frequencies

Now that we have completed our analysis of the fundamental frequencies, we are in a position to consider the assignment of overtones and combination tones. Owing to the fact that the infra-red spectra have been run on the liquid, and that the selection rules for overtones restrict one very little, it is not surprising that a number of weak overtones and combination tones are obtained in the infra-red spectra. The assignment of these, with few exceptions, can be made without difficulty, but under the circumstances the assignment is of no great significance. The frequencies and our suggested assignments are tabulated in Table XII.

The two left-over frequencies which most urgently require explanation are the strong infra-red bands at 1354 cm^{-1} in pyrrole-*N-d* and 1341 cm^{-1} in pyrrole-*d*₅. Any attempt to explain these as N-D fundamentals is ruled out by the complete lack of any frequencies in the 1800-cm^{-1} region in pyrrole and pyrrole-*d*₄. We suggest that they be assigned to $3\nu_{21}$. The corresponding overtone at $2\nu_{21}$ is observed in pyrrole-*N-d*, although it is obscured in pyrrole-*d*₅ by the broad, intense doublet 893-910. 1354 also appears in the Raman effect for pyrrole-*N-d*. This can hardly be explained as $3\nu_{21}$, but it will be noticed that it might well be the combination tone $\nu_{13} + \nu_{21}$.²¹ The broad nature of the Raman band is doubtless due to the fact that two N-H vibrations are involved. A corresponding band might then be expected in the Raman spectrum of pyrrole-*d*₅, but actually none is found. ν_{13} in pyrrole-*d*₅ is interacting strongly with the C-D bending vibrations, and this interaction may lead to a large change in the combination tone's influence on the molecular polarizability.

The only other unassigned frequency of marked intensity is one which occurs in both the infra-red and Raman spectra of pyrrole-*d*₅ at 1147 cm^{-1} . The Raman band is very broad, whereas the infra-red band is quite sharp. This difference leads us to believe that the two should be given different interpretations. A credible interpretation of the Raman frequency would be its assignment to the first overtone of either ν_{22} or ν_{10} . These overtones

²¹ This combination has A_2 symmetry, so that it cannot be used to explain the infra-red band.

have total symmetry and could pick up intensity from the nearby totally symmetrical line at 1084 cm^{-1} . The exactly analogous overtone is observed in the Raman spectrum of benzene-*d*₆. The chief objection to this interpretation is the already mentioned breadth of the Raman band. This breadth might at first be thought to be associated with some N-D vibration, but it is difficult to understand the intensity of this band if it is an overtone or a combination tone without ascribing it to resonance interaction with a nearby fundamental. The only nearby fundamental is the 1084 vibration of class A_1 . No combination tone of total symmetry involving an N-D vibration lies in this neighborhood, and therefore this line probably cannot be ascribed to a combination tone involving an N-D degree of freedom. It seems to us more plausible to suppose that the breadth is due to the presence of several overtones in this neighborhood. At least two of these are totally symmetrical, namely $2\nu_{22}$ and $2\nu_{10}$. Moreover, the combination tone $\nu_{11} + \nu_{21}$, which involves the broad out-of-plane N-D vibration, should also fall hereabouts. Perhaps the net result of these coincidences is their apparent fusion into one broad band. This interpretation is substantiated to some extent by the appearance of a shoulder on the low frequency side of the 1147-cm^{-1} infra-red band in pyrrole-*d*₅. Confirmation from the infra-red spectrum of pyrrole-*d*₄ is difficult because of the presence of the N-H planar bending frequency at 1163 cm^{-1} . There is some sign, however, of a diffuse companion on the high frequency side of the 1094 Raman line in pyrrole-*d*₄. The sharp character of the 1147 band in the infra-red spectrum enables us to make a more definite assertion about its origin. It may very well arise solely from the overtone $2\nu_{22}$. In this case our estimate of ν_{22} in *sym*-pyrrole-*d*₄ and pyrrole-*d*₅ from the product rule calculation will have to be revised downward by 15 cm^{-1} . Clearly experimental determination of this fundamental in the infra-red is most desirable.

The interpretation of the remaining frequencies requires no especial discussion except to remark that assignment of all the left-over frequencies in pyrrole-*d*₄ and pyrrole-*d*₅ is hardly feasible until experimental values are obtained for ν_{18} and ν_{22} .

CONCLUSIONS

From the foregoing discussion it is clear that a postulated symmetry of C_{2v} is quite adequate to explain the spectroscopic results. In particular, the agreement of the frequencies assigned to the A_1 and B_1 classes with the product rule τ 's for these classes is quite satisfactory. Many of the intensity changes attendant upon deuterium substitution are likewise understandable. The question now remains: Will any other symmetry serve equally well to interpret the spectra? Symmetries higher than C_{2v} can be eliminated immediately on the grounds that they are not compatible with chemical evidence and with electron diffraction results. Furthermore, as Reitz⁸ has already pointed out, too many polarized Raman lines are found to allow postulation of a higher symmetry.

There are two possible lower symmetries, C_1 and C_s . C_1 can be excluded, for it demands that all the Raman lines be polarized and this is obviously not the case. To obtain the product rule ratios (τ 's) for C_s symmetry, one merely multiplies together the τ 's for C_{2v} symmetry in the following manner:

$$\begin{array}{ll} \tau : C_s & \tau : C_{2v} \\ A' & A_1 \times B_2 \\ A'' & B_1 \times A_2 \end{array}$$

It is obvious that if the product rule is obeyed for all classes of a C_{2v} symmetry, it will also be obeyed for a C_s symmetry. The converse, however, is not necessarily true. In fact, it seems to us that it would be an improbable accident for the frequencies of a C_s molecule to fit the product rule for each of the four classes of a C_{2v} structure.

The A' frequencies, for example, of a C_s structure are all mechanically interconnected. When one imputes to a C_s molecule a C_{2v} symmetry, one asserts in effect that the A' frequencies can be split into two groups (classes A_1 and B_2 of C_{2v}) which are mechanically independent. Unless the special nature of the C_s molecular potential system is such that this assertion is valid, it is impossible for the frequency changes caused by deuterium substitution to satisfy a product rule for C_{2v} symmetry. Hence, although a C_s symmetry cannot be rigorously excluded on these grounds, it is made most unlikely. This conclusion is given strong support by the number of polarized Raman lines;⁸ thirteen are demanded for C_s symmetry while only eight are found which can be established as fundamentals (Table II). We are, therefore, convinced that pyrrole is a C_{2v} molecule.

As we have remarked earlier, the complete survey of the infra-red spectra down to 400 cm^{-1} , preferably in the vapor, will be necessary before the spectroscopic investigation can be regarded as complete. We hope to carry out such an investigation in the near future if circumstances permit.

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