VIBRATIONAL SPECTRA OF PYRAZOLE IN VARIOUS AGGREGATE STATES AND THEIR INTERPRETATION

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The selection of the fundamental frequencies of pyrazole and the assignment of them to various types of vibrations were made on the basis of a comparison of the IR and Raman spectra of pyrazole and some of its isotopically substituted derivatives in various aggregate states and in the form of complexes with $CdCl_2$. The assignment was confirmed by prior calculation of the frequencies and forms of the vibrations of pyrazole.

We have previously studied the vibrational spectra of polyfunctional pyrazole derivatives that are capable of undergoing tautomeric transformations [1]. In the present research we set out to obtain and interpret the vibrational spectra of pyrazole itself as the principal fragment of the investigated class of compounds.

The assignment of the frequencies in the vibrational spectra of pyrazole [2, 3] and its mono- and polyalkyl derivatives [4, 5] has not yet been effected convincingly. It is known that pyrazole exists as twisted hydrogen-bonded chains in the crystalline state [6] and as cyclic dimers and trimers in solution (CCl_4), even up to concentrations of 10^{-3} to 10^{-4} M [7]. Strong intermolecular hydrogen bonds and the crystal-lattice field complicate the spectrum of pyrazole (as compared with the gas), leading to shifts in the band and splitting of them, as a consequence of which errors may arise in the assignment. Special attention was therefore directed to the recording and interpretation of the spectrum of the isolated monomeric molecule.

In order to select the fundamental frequencies of pyrazole and interpret them we obtain the IR spectra of pyrazole, $^{15}N_2$-pyrazole, 4-D_1-pyrazole, and 3,4,5-D_3-pyrazole in the gaseous and crystalline states; the IR spectra of complexes of the compounds indicated above, and of 1-D_1-pyrazole, 1,4-D_2-pyrazole, and D_4-pyrazole with $CdCl_2$ in the crystalline state; the Raman spectra of pyrazole, $^{15}N_2$-pyrazole, and 1,4-D_2-pyrazole in the crystalline state; the IR spectra of solutions of pyrazole on successive dilution in carbon disulfide and CCl_4 (concentrations from 10^{-1} to 10^{-3} M); and the Raman spectra in CCl_4 (10^{-1} and 10^{-2} M) (Tables 1 and 2 and Figs. 1 and 2).

On the basis of investigations of the microwave spectra it was established that the pyrazole molecule is planar [8, 9] and has C_s point group symmetry; the normal vibrations, with respect to symmetry types, are distributed as follows: $\Gamma = 15A' + 6A''$. In the spectrum of the gas, bands of the C form with an intense Q branch and a distance of 40 cm^{-1} between the P and R branches should correspond to six vibrations of the A'' type, and bands of the A and B forms with a distance of 24 cm^{-1} between the P and R branches should correspond to 15 planar vibrations of the A' type (see [2]).

Five bands of vibrations of the A'' type – 515, 670, 746, 833, and 880 cm^{-1} – are readily isolated in the spectrum of the gas (Table 1). In conformity with [10] and also in analogy with imidazole [11], we assigned the first band to the γ_{NH} vibration. As in [2], the bands at 746, 833, and 880 cm^{-1} were assigned to the γ_{CH} vibrations, while the band at 670 cm^{-1} was assigned to ring deformation (γ ring). The six vibrations of the A'' type should probably appear at 600-650 cm^{-1}, as in the case of imidazole [11]. It should be noted that one of the intense bands in the spectrum of crystalline pyrazole (612 cm^{-1}) cannot be considered

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TABLE 1. Vibrational Spectra of Pyrazole in Various Aggregate States (frequencies, cm^{-1})*

Gas	Solutions†					Crystal	
	10^{-1} *M*		10^{-2} *M*		10^{-3} *M*		
IR	IR	Raman	IR	Raman	IR	IR	Raman
492							
501							
515	530 w	523	530 m		530 s	612 s	627
535	612 m		611 w				
538		584					
650							
672	670 w	670			672 s	652 w	
695							
728							
746	755 s		752 s		750 s	760 s	782
767							
815							
833						835 s	840
856							
880	882 s	876				875 s	880
896						890 s	
910	917	915		910		915 s	917
920	934	928		966		935 s.	944
997							
1010	1038 s	1035	1038	1001	1017 s	1030 s	1037
1020	1050 s	1048	1050	1056			1050
1060	1092 m	1066		1064		1055 s	1059
1115							
1125	1140 s		1125 s		1123 s	1137 s	
1140	1156 s	1152		1155		1155 m	1150 s
1245		1218		1218		1227 w	
1270	1260 w	1258		1258		1260 m	1270 s
1340		1322		1322			
1360	1360 m	1354	1345	1354	1347	1360 m	1366 m
1387					1377		
1410	1395 s	1392	1395 s	1395	1395 s	1400 s	1407 m
1442			1430 w		1430 w		
1470	1450 m	1470	1450 m			1470 m	
	1480 m		1475 m	1470			
1525						1530 w	
1555						1550 w	
3115							
3125							
3140							
3510							
3525							
3535				3485			

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*The abbreviations used here and elsewhere are as follows: s is strong, m is medium, and w is weak.

†The 400-1300 cm^{-1} and 1250-1450 cm^{-1} ranges were investigated for solutions in CS_2 and CCl_4, respectively.

to be γ-ring vibration (A″) [2], inasmuch as it vanishes in the spectrum of solutions (CS_2) on dilution with the simultaneous development of a band at 530 cm^{-1} (Table 1), which corresponds to γ_{NH} vibration (515 cm^{-1} in the gas). The character of the shift of this band on weakening of the hydrogen bond, in the order crystal, complex, solution, gas (612, 593, 530, and 515 cm^{-1}), confirms its assignment to the γ_{NH} vibration. Unfortunately, we were unable to follow the isotopic shift of the 515 cm^{-1} band in the spectrum of 1-D_1-pyrazole gas. As in the case of imidazole [11], as a consequence of the high lability of the hydrogen atom attached to the nitrogen, there is rapid reversible exchange of deuterium by hydrogen. The spectra of the complexes are of substantial assistance in the assignment. The lability of the hydrogen atom is reduced in complexes, for example, with $CdCl_2$ owing to the strong hydrogen bond with the anion [12]; this makes it possible to obtain 1-deutero derivatives of pyrazole with a high percentage of deuterium in the 1-position. An additional advantage of the spectra of the complexes as compared with the spectra of crystals is the presence at 800-950 cm^{-1} of narrow, nonoverlapped bands, which can be compared with the corresponding bands in the spectrum of the gas, and the absence of broad intense bands at 2800-3300 cm^{-1}. Thus, the shift in the γ_{NH} vibrational bands during deuteration – γ_{NH} 593 cm^{-1}, γ_{ND} 480 cm^{-1} (Fig. 2) – can be followed by comparison of the spectra of complexes of pyrazole and 1-D_1-pyrazole. We note that replacement of the hydrogen in the 4, 3, and 5 positions by deuterium has virtually no effect on the γ_{ND} vibrational frequencies (478 cm^{-1}) (Fig. 2).

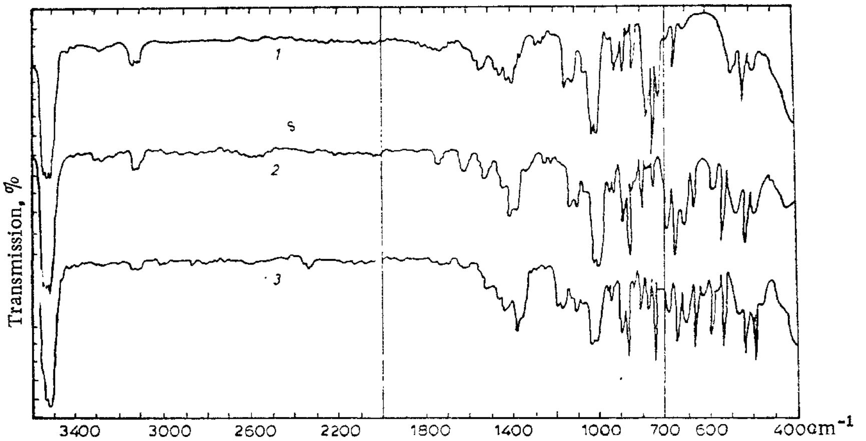

Fig. 1. IR spectra in the gaseous state: 1) pyrazole; 2) 4-D_1-pyrazole; 3) 3,4,5-D_3-pyrazole (3,4-D_2-pyrazole and 4,5-D_2-pyrazole impurities are present).

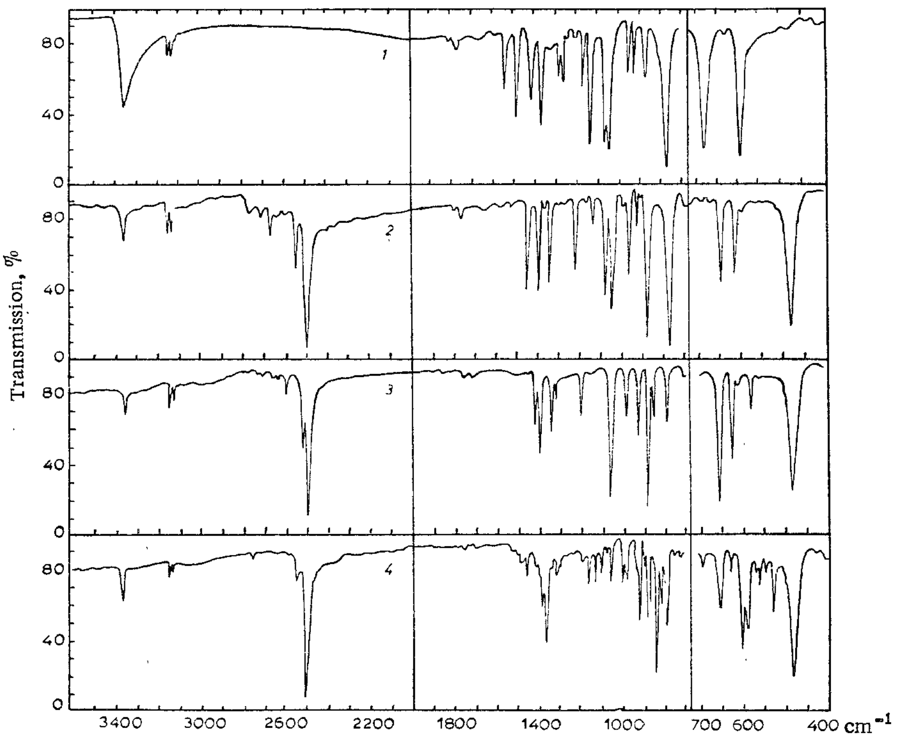

Fig. 2. IR spectra of complexes with $CdCl_2$: 1) pyrazole; 2) 1-D_1-pyrazole; 3) 1,4-D_2-pyrazole; 4) D_4-pyrazole (1,3,4,-D_3-pyrazole and 1,4,5-D_3-pyrazole impurities are present).

The assignment of the in-plane vibrations (A') present considerable difficulty, and their interpretation can only be carried out by simultaneous study of the IR and Raman spectra in various aggregate states with correlation of the bands from the spectra of the complexes.

The ν_{NH} and ν_{CH} vibrations are most readily identified. The ν_{NH} band has a frequency of 3525 cm^{-1} in the spectrum of the gas and 3485 cm^{-1} in the spectrum of a solution (CCl_4). The ν_{CH} vibrations in the gas give a weak, broad band at 3115-3140 cm^{-1} (Fig. 1) but appear as three narrow bands at 3125, 3140, and 3155 cm^{-1} in the spectra of the complexes (Fig. 2).

Of the five ring vibrations, four should apparently be observed at 1200-1600 cm^{-1}. The bands at 1470, 1400, 1350, and 1255 cm^{-1} can be adopted as the fundamental frequencies (Table 1). In contrast to [2], we are inclined to consider the band at 1525 cm^{-1} (pyrazole complex, Table 2) as a composite band 939 + 593 (γ_{NH}), inasmuch as it does not appear in the spectrum of the 1-D_1-pyrazole complex, while the remaining

TABLE 2. IR Spectra of Complexes of Pyrazole and Its Isotopically Substituted Derivatives with $CdCl_2$ (frequencies, cm^{-1})

Pyrazole	$^{15}N_2$-Pyrazole	1-D_1-Pyrazole	4-D_1-Pyrazole	1,4-D_2-Pyrazole	3,4,5-D_3-Pyrazole*	D_4-Pyrazole†
		480 s		480 s		477 s
					521 s	523 m
					535 m	
				578 w	555 w	583 s
	583 s				575 w	
593 s					587 s	598 s
		612 m	600 s			
630 w	627 w	645 m	638 m	623 m		
				652 s		650 m
678 w	673 s	—	682 s			695 w
763 s	762 s	761 s	—	—	672 s	—
			783 w	780 m	—	787 m
					790 m	813 m
						835 s
			850 w	850 w	840 855 w	
860	860					866 875 w
865	865	870 s	873 s	870 s	866	
					875 m	
916 w	912 w	920 w	903 w	915 m	885	915 m
939	925				900 910 m	
			965 s	965 975 w	965 980 m	977 990 w
1041 s	1030 s	1038 s	1040 s	1050 s		1050 w
1055 s	1050 s	1055 m			1043 s	
		1068 s				
					1090 s	1100 w
						1120 w
1128 s	1123 s	1127 w	1123 s			
					1122	1135 w
	1142 m		1150 s		1135 m	
1160 m		1160 w			1145	
				1191 m		1185 w
		1212 m			1185 s	
1255 w	1245 m		1245 m			
					1232 1245 w	1260 s
1270 w	1263 w					1275 m
	1345 s	1336 s	1340 m	1333 m		1310 w
1358 s						1360 s
	1395 m	1385 s	1395 s	1388 s	1365 m	1375 m
1405 m				1405 m	1385 1400 m	
		1435 s				1452 w
	1457 s		1463 m			
					1450 m	
1475 s					1460 w	
1525 m	1523 m	—	1515 m		1483 m	
					1500 m	
					1555 w	
		2500 s		2500 s		2503 s
		2540 w		2520 m		2544 w
3125	3120			2595 w		
3135 w	3135 w	2663 w	3135 3150 w			
3155	3150	3120				
3358 s	3350 s	3135 w	3355 s	3130 3150 w	3355 s	
		3150				

*A mixture of 3,4-D_2-pyrazole and 4,5-D_2-pyrazole.

†A mixture of 1,3,4-D_3-pyrazole and 1,4,5-D_3-pyrazole.

four bands are shifted by 10-30 cm^{-1} to lower frequencies. The band at 1152 cm^{-1}, which is the most intense in the Raman spectrum of pyrazole and the weakest in the IR spectrum of the gas, may be the fifth band affiliated with the ring vibrations. The bands observed in the Raman spectrum at 1258 and 1152 cm^{-1} are polarized. The assignment of the five bands under discussion to the ring vibrations is arbitrary, inasmuch as in the deuterium derivatives they experience strong shifts; this indicates the complex character of these vibrations (they are shifted with the δ_{NH} and δ_{CH} deformation vibrations). We assign the bands at 1125 and 1060 and at 1010 cm^{-1} (gas) to the δ_{NH} and δ_{CH} deformation vibrations. Actually the band at 1127 cm^{-1} in the spectrum of the pyrazole complex is related to the δ_{NH} vibration, inasmuch as it is shifted to 870 cm^{-1} in the spectrum of 1-D_1-pyrazole (Fig. 2). The δ vibrations apparently show up at 1000-1060 cm^{-1}, as indicated by the decrease in intensity of the corresponding band on successive replacement of the hydrogen by deuterium.

The remaining two A' vibrations (ring δ) probably should be sought at 850-940 cm^{-1}, in analogy with imidazole [11]. The bands at 910 cm^{-1} (gas) and 940 cm^{-1} (complex) can be assigned to one of them. The second δ ring band is possibly masked by the P and R branches of the bands at 833 and 880 cm^{-1} (γ_{CH}), and, in conformity with imidazole [11], we assume it to be 865 cm^{-1}.

TABLE 3. Assignment of the Fundamental Frequencies in the Vibrational Spectra of Pyrazole

Symmetry type	Observed frequency, cm^{-1}	Calculated frequency, cm^{-1}	Assignment
A''	515	515	γ_{NH}, γ ring, , $\gamma_{CH_{(4)}}$
	615	619	γ ring, γ_{CH}
	670	668	γ ring, γ_{CH}
	746	744	$\gamma_{CH_{(4)}}$, γ_{NH}
	833	831	$\gamma_{CH_{(5)}}$
	880	886	$\gamma_{CH_{(3)}}$
A'	865	870	δ ring, δ_{CH}
	910	915	δ ring
	1010	998	$\delta_{CH_{(3)}}$, δ_{NH}
	1030	1011	$\delta_{CH_{(5)}}$
	1060	1053	$\delta_{CH_{(4)}}$, δ_{NH}
	1125	1120	δ_{NH}, $\delta_{CH_{(4)}}$
	1152	1155	ν ring, δ_{NH}
	1258	1263	ν ring, δ_{CH}
	1350	1349	ν ring, δ_{NH}, δ_{CH}
	1400	1406	ν ring, δ_{CH}, δ_{NH}
	1470	1483	ν ring, δ_{CH}
	3125	3128	$\nu_{CH_{(4)}}$
	3135	3138	$\nu_{CH_{(3)}}$
	3155	3152	$\nu_{CH_{(5)}}$
	3525	3520	ν_{NH}

The assignment that we made on the basis of a study of the IR and Raman spectra of pyrazole in various aggregate states and a comparison with the spectra of complexes of isotopically substituted pyrazole was confirmed by a preliminary calculation of the frequencies and forms of the normal vibrations. The results of the calculation and the assignment of the fundamental frequencies are presented in Table 3.* The calculation showed that almost all of the vibrations of pyrazole except for the ν_{CH} and ν_{NH} stretching vibrations are composite. An examination of the forms of the vibrations confirmed that the δ_{CH} and δ_{NH} vibrations make a significant contribution to the ring vibrations and that the δ_{NH} vibration is mixed with almost all of the δ_{CH} vibrations.

EXPERIMENTAL

Pyrazole and $^{15}N_2$-pyrazole were obtained by the method in [13].

1,4-D_2-Pyrazole. A solution of 1 g (0.015 mole) of pyrazole in 15 ml of D_2O and 1 ml of D_2SO_4 was heated in an ampoule in an autoclave at 100° for 16 h, after which half the original volume of D_2O was removed by vacuum distillation. The residue was neutralized with NaOD solution and extracted with ether. The ether solution was thoroughly vacuum evaporated, and the residue was purified by double vacuum sublimation to give 0.72 g (72%) of product.

D_4-Pyrazole. A solution of 0.7 g (0.01 mole) of 1,4-D_2-pyrazole and sodium methoxide (from 14 ml of CD_3OD and 0.3 g of Na) was heated in an ampoule in an autoclave at 100° for 22 h, after which the CD_3OD was removed by distillation, and the residue was dissolved in D_2O. The solution was neutralized with D_2SO_4 and extracted with ether. The ether solution was thoroughly vacuum evaporated, and the residue was purified by vacuum sublimation. The yield of D_4-pyrazole was 0.43 g (60%).† The degree of replacement of hydrogen by deuterium was evaluated by means of the PMR spectra.

The complexes of pyrazole and its isotopically substituted derivatives with $CdCl_2$ were obtained by mixing solutions for H_2O or D_2O (the $CDCl_2$-to-pyrazole ratio was 1 : 2). Found: C 17.9; Cl 22.0%. $2C_3H_4N_2 \cdot CdCl_2$. Calculated: C 17.5; Cl 22.2%.

The IR spectra of pyrazole, its isotopically substituted derivatives, and their complexes were recorded with a UR-10 spectrometer. The spectra of crystalline samples were recorded from KBr pellets.

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*The assignment was confirmed by calculation of isotopically substituted pyrazole. The details involved in the calculation, the method used to select the force field, and the final set of force constants will be presented in our next paper.

†According to microwave [9] and mass spectrometric data, the sample also contained 1,3,4-D_3-pyrazole and 1,4,5-D_3-pyrazole in addition of D_4-pyrazole.

The spectra of solutions of pyrazole in CCl_4 and CS_2 were recorded during successive dilution from 10^{-1} to 10^{-3} M and while the layer thickness was increased from 0.1 to 50 mm. The spectra in the gaseous state were obtained at 100° and a pressure of 10 mm with the use of a 100-cm long multiple-pass gas cuvette. The Raman spectra of the pyrazole solutions were obtained with a 100-cm long cuvette and a DFS-2 spectrometer with photographic recording [exposures of 75 h (10^{-1} M) and 125 h (10^{-2} M)] and a powerful low-pressure mercury lamp [14]. The Raman spectra of crystalline samples were obtained with a Cary 81 spectrometer with an argon laser.

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