

IN PLANE VIBRATIONS OF PYRIMIDINE AND SOME DEUTERATED
PYRIMIDINES

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ABSTRACT

On the basis of 102 assigned frequencies to in plane vibrations of pyrimidine, pyrimidine-2-d₂, pyrimidine-2,5-d₂, pyrimidine-4,6-d₂, pyrimidine-2,4,6-d₃ and pyrimidine-d₄, 35 valance force field constants including 14 principals and 21 interaction force constants are calculated. New assignments are suggested for ν_{18b} and ν_{19b} normal modes in pyrimidine-2,5-d₂ and ν_{14} and ν_{18b} normal modes in pyrimidine-d₄.

With this new assignments the agreement between observed and calculated product rule and sum rule has improved.

INTRODUCTION

Vibrational spectra of pyrimidine has been studied by many investigators [1-4]. On the basis of assigned frequencies Berzine et al[5] and Patine et al[6] have calculated the force field constants of pyrimidine and pyrimidine-d₄. Sarma[1] has calculated in plane force field constants for in plane vibrations of these molecules. Milani-nejad and Stidham [8] have studied the Raman spectra of pyrimidine, pyrimidine-2-d₁, pyrimidine-2,5-d₂, pyrimidine-4,6-d₂, pyrimidine-2,4,6-

d₃ and pyrimidine-d₄ in liquid phase and the IR spectra in vapor and liquid phases. Sarma has used 8 principals and 4 interaction force constants derived from his previous calculation [7] to determine the in plane vibrations frequencies of pyrimidine-2-d₁, pyrimidine-2,5-d₂, pyrimidine-4,6-d₂ and pyrimidine-2,4,6-d₃, and also to predict the in plane vibrational frequencies of pyrimidine-5-d₁ and pyrimidine-4,5,6-d₃[9]. Sarma has criticized some of the Milani-nejad et al, assignments (three in pyrimidine-2-d₁,

five in pyrimidine-2,5-d₂, two in pyrimidine-4,6-d₂ and three in pyrimidine-2,4,6-d₃). His criticism is based on the mistaken assumption that substitution of hydrogen with deuterium only shifts CH stretching and bending frequencies while according to non-crossing rule in isotopic substitution the frequencies in a symmetry representation do not cross [10].

FORCE FIELD CALCULATIONS AND DISCUSSION

The molecular geometry of pyrimidine has been determined by X-Ray crystallography[11] and by microwave spectroscopy[12]. The molecule is planar and belongs to C_{2v} point

group. Substitution of hydrogen with deuterium in positions(2),(2,5),(4,6),and(2,4,6)retains the C_{2v} symmetry. (Pyrimidine-5-d₁ and pyrimidine-4,5,6-d₃ also belongs to C_{2v} symmetry point group, but due to lack of experimental information they are not included in these calculations).

24 vibrational modes are distributed among vibrational representation as 9A₁+2A₂+8B₁+5B₂. A₁ and B₁ are the in plane, and A₂ and B₂ are the out of plane vibrations:

Geometry assumed in these calculations which are extracted from references[11]and[12],are listed in table 1, and the 24 in plane internal coordinates are defined in Fig.1. Symmetry coordinates are summarized

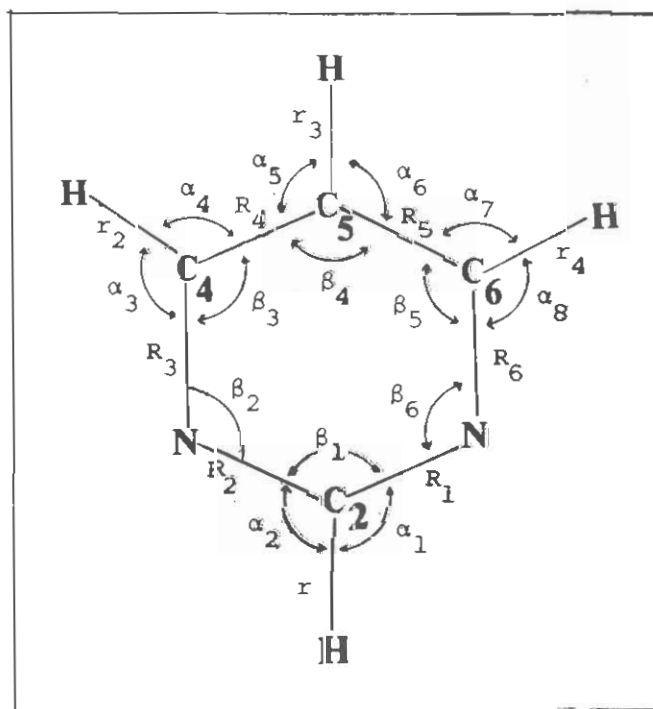


Fig.1- In plane internal coordinates for pyrimidine.

Table 1: Assumed geometry for pyrimidine

r_2 (CH)	1.080 Å	$r(2C-N)$	1.315 Å	NCN angle	128.20°
r_4 (CH)	1.085 Å	$r(4C-N)$	1.337 Å	CNC angle	115.15°
r_5 (CH)	1.090 Å	$r(C-C)$	1.372 Å	NCC angle	116.30°

Table 2: Symmetric coordinates for in plane vibrations of pyrimidine

	$S_1 = r_1$	$S_8 = \frac{1}{\sqrt{2}}(\alpha_3 + \alpha_8)$
	$S_2 = \frac{1}{\sqrt{2}}(r_2 + r_4)$	$S_9 = \frac{1}{\sqrt{2}}(\alpha_4 + \alpha_7)$
	$S_3 = r_3$	$S_{10} = \frac{1}{\sqrt{2}}(\alpha_5 + \alpha_6)$
A_1	$S_4 = \frac{1}{\sqrt{2}}(R_1 + R_2)$	$S_{11} = \beta_1$
	$S_5 = \frac{1}{\sqrt{2}}(R_3 + R_6)$	$S_{12} = \frac{1}{\sqrt{2}}(\beta_2 + \beta_6)$
	$S_6 = \frac{1}{\sqrt{2}}(R_4 + R_5)$	$S_{13} = \frac{1}{\sqrt{2}}(\beta_3 + \beta_5)$
	$S_7 = \frac{1}{\sqrt{2}}(\alpha_1 + \alpha_2)$	$S_{14} = \beta_1$
	$S_{15} = \frac{1}{\sqrt{2}}(r_2 - r_4)$	$S_{20} = \frac{1}{\sqrt{2}}(\alpha_3 - \alpha_8)$
	$S_{16} = \frac{1}{\sqrt{2}}(R_1 - R_2)$	$S_{21} = \frac{1}{\sqrt{2}}(\alpha_4 - \alpha_7)$
B_1	$S_{17} = \frac{1}{\sqrt{2}}(R_4 - R_5)$	$S_{22} = \frac{1}{\sqrt{2}}(\alpha_5 - \alpha_6)$
	$S_{18} = \frac{1}{\sqrt{2}}(R_4 - R_3)$	$S_{23} = \frac{1}{\sqrt{2}}(\beta_2 - \beta_6)$
	$S_{19} = \frac{1}{\sqrt{2}}(\alpha_1 - \alpha_2)$	$S_{24} = \frac{1}{\sqrt{2}}(\beta_3 - \beta_5)$

in table 2.

Willson g matrix in internal coordinates and 35 valance force field including 14 principals and 21 interaction force constants are transferred to G and F matrices by a U matrix which is constructed from the coefficients of symmetric coordinates.

$$G = U g U'$$

$$F = U f U'$$

Where U' is transpose of U . 5 redundant symmetric coordinates in A_1 and 2 in B_1 representations are eliminated after this transformations.

Principal force constants includes Kr_1, Kr_2 and Kr_3 for C-H stretches; K_{R1}, K_{R2} , and K_{R3} for C_2-N , C_6-N and C_4-N and C-C stretches; four H_α 's for in plane CH bendings and four H_β , for in plane ring bendings.

Shacht-Schinder programs [13] have been used to obtain a least square fit to the 102 assigned frequencies assigned to in plane vibrations of pyrimidine, and deuterated pyrimidine, by Milani-nejad et al [8]. The best fit produces the frequencies with the average error of 4.5, 6.5, 12.3, 5.0, 8.0 and 14.8 cm^{-1} for pyrimidine, pyrimidine-2-d₁, pyrimidine-2,5-d₂, pyrimidine-4,d-d₂, pyrimidine-2,4,6-d₃ and pyrimidine-d₄, respectively, relatively large error for pyrimidine-2,5-d₂ and pyrimidine-d₄ indicates that some of the assigned frequencies in B₁ representation for these two molecules are incorrect.

Undoubtedly, assignment of 1325 cm^{-1} band of pyrimidine-2,5-d₂ to ν_{19b} normal mode is incorrect. This band in pyrimidine and other deuterated pyrimidines appears at frequencies higher than ν_{19a} . Thus we assign the 1435 cm^{-1} band at the shoulder of 1388.5 cm^{-1} band in the liquid phase IR spectrum of pyrimidine-2,5-d₂ to ν_{19b} normal mode and the shoulder at 845 cm^{-1} to in plane CD bending instead of the shoulder at 950 cm^{-1} .

Milani-nejad et al [8] tentatively assigned the weak band at 1114 cm^{-1} in Raman spectrum of pyrimidine-d₄ to ν_{14} normal mode. Calculations show that this mode should appear around 1156 cm^{-1} . Sebrana et al [4] reported a weak band at 1165 cm^{-1} in solid

phase spectrum of pyrimidine-d₄. We tentatively assign this band to ν_{14} mode and 845 cm^{-1} band in IR spectrum to CD bending.

With these new assignments the adjusted, force constants (Table 3) give the calculated frequencies (Table 4) with an average error of 4.5, 5.1, 5.1, 4.5, 4.9 and 5.4 cm^{-1} for pyrimidine, pyrimidine-2-d₁, pyrimidine-2,5-d₂, pyrimidine-4,6-d₂, pyrimidine-2,4,6-d₃ and pyrimidine-d₄, respectively. The ratio of products of frequencies of pyrimidine-2,5-d₂ and pyrimidine-d₄ to the products of frequencies of pyrimidine in B₁ representation are 0.514 (theoretical value 0.524) and 0.720 (theoretical value 0.276), respectively. The sum rule [14] for B₁ representation are:

$$\begin{aligned} \sigma_{\text{pyrimidine}} + \sigma_{\text{pyrimidine-d}_4} &= \sigma_{\text{pyrimidine-2-d}_1} + \sigma_{\text{pyrimidine-4,6-d}_2} \\ 34.74 &= 34.73 \quad \Delta = 0.03\% \\ \sigma_{\text{pyrimidine}} + \sigma_{\text{pyrimidine-2,4,6-d}_3} &= \sigma_{\text{pyrimidine-2-d}_1} + \sigma_{\text{pyrimidine-4,6-d}_2} \\ 34.74 &= 34.73 \quad \Delta = 0.03\% \\ \sigma_{\text{pyrimidine-2-d}_1} + \sigma_{\text{pyrimidine-d}_4} &= \sigma_{\text{pyrimidine-2,5-d}_2} + \sigma_{\text{pyrimidine-2,4,6-d}_3} \\ 33.99 &= 33.12 \quad \Delta = 0.09\% \end{aligned}$$

$$\text{Where: } \sigma \times 10^{-6} = 4\pi^2 \sum_k \nu_k^2 = 4\pi^2 C^2 \sum_k \nu_k^2$$

and K is the number of normal modes in each representations. In the above calculations the constant $4\pi^2 C^2$ is eliminated from both sides of the equality.

Table 3: Valance force field constants for in plane vibrations of pyrimidine.

Force constant	Description		Value	
Kr ₁	C ₂ -H	st	5.025	
Kr ₂	C ₄ -H	st	5.068	
Kr ₃	C ₅ -H	st	5.068	
KR ₁	C ₂ -N	st	6.720	
KR ₂	C ₄ -N	st	5.591	
KR ₃	C-C	st	5.162	
Ha ₁	H-C ₂ -N	bend	0.578	
Ha ₂	H-C ₄ -N	bend	0.559	
Ha ₃	H-C ₄ -C	bend	0.553	
Ha ₄	H-C ₄ -C	bend	0.551	
Hβ ₁	N-C ₂ -N	bend	1.870	
Hβ ₂	C ₂ -N-C ₄	bend	1.496	
Hβ ₃	N-C-C	bend	1.059	
Hβ ₄	C-C-C	bend	1.050	
FRR' ₁	C ₂ -N	st / C ₂ -N	st	1.251
FR ₁ R ₂	C ₂ -N	st / C ₄ -N	st	1.105
FR ₁ R ₃	C ₄ -N	st / C ₂ -N	st	0.935
FR ₂ R ₃	C-C	st / C-N	st	0.817
FR ₁ α ₁	C ₂ -N	st / H-C ₂ -N	bend	0.519
FR ₂ α ₂	C ₂ -N	st / H-C ₄ -N	bend	0.330
FR ₃ α ₃	C-C	st / H-C ₄ -N	bend	0.184
FR ₃ α ₄	C-C	st / H-C ₅ -N	bend	0.157
Fα ₁ β ₁	H-C-N	bend/ N-C-N	bend	-0.310
Fα ₂ β ₃	H-C ₄ -N	bend/ N-C-C	bend	-0.216
Fα ₃ β ₃	H-C ₄ -C ₅	bend/ N-C-C	bend	-0.147
Fα ₄ β ₄	H-C ₅ -C ₄	bend/ C-C-C	bend	-0.226
Fβ ₁ β ₂	N-C ₂ -N	bend/ C-N-C	bend	0.657
Fβ ₂ β ₃	C-N-C	bend/ N-C-C	bend	0.304
Fβ ₃ β ₄	N-C-C	bend/ C-C-C	bend	0.211
Fβ ₁ β ₃	N-C-N	bend/ N-C-C	bend	0.505
Fβ ₂ β' ₂	C ₂ -N-C ₄	bend/ C ₂ -N-C ₆	bend	0.538
Fβ ₃ β' ₃	N-C ₂ -C	bend/ N-C-C	bend	0.515
Fβ ₁ β ₄	N-C-N	bend/ C-C-C	bend	0.709
Fβ ₂ β ₃	C-N-C	bend/ N-C-C	bend	0.680
Fβ ₂ β ₄	C-N-C	bend/ C-C-C	bene	0.513

Table 4: Calculated and observed frequencies for pyrimidine and deuterated pyrimidines (cm^{-1}).

pyrimidine-d ₄		pyrimidine-2,4,6-d ₃		pyrimidine-4,6-d ₂		pyrimidine-2,5-d ₂		pyrimidine-2-d ₁		pyrimidine		Vibrational		Symmetry	
calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	No.	Type	species	
2296	2295	3061	3061	3068	3078	3041	3033	3068	3074	3074	3074	3074	CH st	20a	
2271	2275	2271	2268	3040	3047	2295	2276	3034	3038	3041	3052	3041	CH st	2	
2267	2262	2269	2268	2273	2272	2268	2268	2272	2267	3034	3034	3034	CH st	13	
1517	1527	1535	1535	1539	1535	1550	1551	1573	1560	1575	1567	1575	Ring	8a	
1274	1275	1281	1283	1301	1295	1386	1388	1386	1393	1399	1398	1399	Ring	19a	
1048	1042	1053	1045	1065	1061	1104	1109	1110	1115	1135	1139	1135	Ring+	9a	A ₁
	974	975	989	994	989	1050	1055	1053	1075	1058	1065	1058	Ring+	12	
													CH st		
876	860	856	865	886	874	979	976	988	990	998	992	998	Ring	1	
654	657	660	665.5	665	669	661	664	671	673	678	678	678	Ring	6a	
2294	2300	2294	2300	2294	2305	3077	3074	3077	3074	3077	3086	3077	CH st	7b	
1522	1536	1555	1548	1555	1555	1531	1536	1575	1564	1575	1568	1575	Ring	8b	
1330	1327	1403	1397	1439	1466	1435	1435*	1438	1438	1458	1466	1458	Ring	19b	
1157	1165*	1185	1177	1310	1305	1269	1265	1272	1271	1369	1370	1369	Ring	14	B ₁
940	985	1122	1125	1173	1177	1153	1162	1173	1162	1233	1225	1233	CH bend	3	
898	907	955	944	1081	1074	923	910	1115	1115	1158	1159	1158	CH bend	15	
850	845*	905	912	918	916	856	845*	933	944	1073	1071	1073	CH bend	18b	
611	603	611	610	612	612	626	618	620	622	620	623	620	Ring	6b	

* Assignments have been changed, see the text.

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