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Analysis of UV absorption spectra of 2,4-and 4,6-dichloropyrimidine vapours

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The UV absorption spectra of 2,4- and 4,6-dichloropyrimidine vapours pertaining to an allowed A'–A' and A_1–B_1 transitions respectively (analog of $^1B_1$ $\pi^*, n)$–$^1A_1$ transition of pyrimidine around 3200Å) are reported in this paper The absorption system appearing in the region λλ3075–2815 in 2,4-dichloropyrimidine with 0, 0 band at 33121 cm^{-1} and λλ3010–2760 in the 4,6-dichloropyrimidine with 0, 0 band at 34788 cm^{-1} are analysed in terms of the vibrational frequencies of the ground and the excited electronic state In the absence of the Raman spectra, the observed frequencies of the two molecules are correlated with the infrared frequencies*

1. INTRODUCTION

The ultraviolet absorption spectra of pyrimidine presents a stronger absorption system around 2430Å and a weaker system around 3200Å. Since the stronger absorption system (analog of 2400Å system of benzene) does not show any vibrational structure, no vibrational analysis has been reported. The less intense system appearing around 3200Å contains a large number of discrete bands and a vibrational analysis has been proposed by Uber (1941) The rotational analysis of the 0, 0 band of this system by Innes *et al.* (1969) reveals that this system appears due to $\widetilde{A}^1B_1$–$\widetilde{X}^1A_1$ transition. The present work aims at (1) to study the spectral shift produced in the 0, 0 band of the 3200Å system of pyrimidine by strongly interacting substituents (2) to classify the vibrational frequencies of the two states and (3) to propose the model assignment of the observed frequencies.

2. EXPERIMENTAL PROCEDURE

2,4- and 4,6-dichloropyrimidine obtained from M/S Fluka, A.G Switzerland were used as such. Vapour absorption spectra appearing in the regions λλ3075–2815 and λλ3010–2760 in the two molecules have been photographed on Hilger medium quartz spectrograph using path lengths of 50, 75, 100 and 150 cms

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* Unpublished work.

Sufficient number of bands have been obtained with a small quantity of sample placed in an absorption tube of length 100 cm The temperature of the absorption column was varied from 20°C to 100°C Hilger comparator having least count of 0.001 mm was used for evaluating the position of the bands The

Table 1 Vibrational analysis of 2,4- dichloropyrimidine vapour (All values are in cm^{-1})

λ_{air} Å	$\nu_{vac.}$	Intensity$^+$	Separation from the 0, 0 band	Assignment
3072.2	32541	vw	0−580	0−441−2×68
3065.6	32611	wb	0−510	0−441−68
3059.1	32680	mb	0−441	0−441
3031.2	32981	wb	0−140	0−2×68
3024.6	33053	mb	0−68	0−68
3018.4	33121	msd	0, 0	0, 0
3011.2	33200	mw	0+79	0+79
3004.3	33276	wd	0+155	0+2×79
2997.6	33350	vw	0+229	0+3×79
2991.5	33418	wb	0+297	0+434−2×68
2985.3	33488	msd	0+367	0+434−68
2979.3	33555	msd	0+434	0+434
2972.2	33635	wb	0+514	0+434+79
2967.3	33691	mw	0+570	0+570
2962.5	33745	wb	0+624	0+691−68
2956.7	33812	md	0+691	0+691
2952.2	33863	md	0+742	0+801−68
2947.1	33922	msd	0+801	0+801
2940.9	33993	md	0+872	0+801+79
2933.3	34081	wd	0+960	0+801+2×79
2929.7	34123	wd	0+1002	0+434+570
2925.2	34176	md	0+1055	0+1119−68
2919.7	34240	sd	0+1119	0+1119
2915.3	34292	wd	0+1171	0+434+801−68
2912.6	34323	wd	0+1202	0+1119+79
2910.1	34353	sd	0+1232	0+434+801
2903.5	34431	wd	0+1310	0+434+801+79
2900.4	34468	wd	0+1347	0+1483−2×68
2895.2	34530	md	0+1409	0+1483−68
2889.0	34604	msd	0+1483	0+1483
2883.1	34675	md	0+1554	0+434+1119
2878.7	34728	wd	0+1607	0+2×801
2872.1	34808	wd	0+1687	0+2×801+79, 0+570+1119
2867.5	34863	wd	0+1742	0+1119+691−68
2862.1	34929	wd	0+1808	0+1119+691
2858.3	34976	wd	0+1855	0+1119+801−68
2853.2	35038	md	0+1917	0+1119+801
2846.6	35119	wd	0+1998	0+1119+801+79
2843.6	35156	wd	0+2035	0+2×801+434
2836.8	35241	wd	0+2120	0+2×801+434+79
2827.9	35352	md	0+2231	0+2×1119
2820.8	35441	wd	0+2320	0+2×1119+79

b = broad, d = diffuse, m = medium, s = strong, v = very, w = weak.

location of sharp and strong bands are accurate to ± 5 cm^{-1}, while those for the broad and diffuse bands, the accuracy is up to ± 10 cm^{-1}. The position of the bands in cm^{-1}, their visually estimated intensities, their separation from the 0, 0 band and the assignments are presented in tables 1 and 2 for the two molecules respectively.

Table 2. Vibrational analysis of 4,6- dichloropyrimidine vapour (All values are in cm^{-1})

λ_{atr} Å		Intensity†	Separation from the 0, 0 band	Assignment
3008.7	33217		0−1571	0−703−867
2994.0	33390		0−1398	0−526−867
2979.5	33553		0−1235	0−526−703
2966.9	33695		0−1093	0−392−703
2963.1	33739		0−1049	0−2×526
2957.0	33808		0−980	0−2×526+72
2947.2	33921	mb	0−867	0−867
2945.7	33938		0−850	0−2×392+72
2940.3	34000		0−788	0−2×392, 0−703−95
2933.3	34085		0−703	0−703
2027.4	34150		0−638	0−703+72
2922.4	34208		0−580	0−703+130
2917.8	34262	mb	0−526	0−526
2911.4	34338	w	0−450	0−526+72
2906.5	34396	mb	0−392	0−392
2900.5	34467		0−321	0−392+72
2896.2	34518		0−270	0−170−95
2887.8	34618	sb	0−170	0−170
2882.6	34693	mb	0−95	0−95
2873.7	34788	vsd	0, 0	0, 0
2867.8	34860		0+72	0+72
2863.0	34918		0+130	0+130
2858.8	34969	msd	0+181	0+181
2853.0	35041	w	0+253	0+181+72
2850.7	35069	mb	0+281	0+281
2844.8	35141		0+353	0+281+72
2836.4	35246		0+458	0+458
2830.9	35314		0+526	0+458+72
2826.9	35364		0+576	0+458+130
2822.2	35423		0+635	0+181+458
2817.5	35482	md	0+694	0+694
2807.5	35608		0+820	0+694+130
2802.7	35759		0+971	0+281+694
2794.7	35771		0+983	0+1157−170, 0+281+694
2787.9	35858		0+1070	0+1157−95
2781.2	35945		0+1157	0+1157
2776.3	36008		0+1220	0+1157+72
2771.8	36067		0+1279	0+1157+130
2766.8	36132		0+1344	0+1157+181

† As in table 1.

3. Discussion

From the structural point of view, the two molecules i.e., 2,4- and 4,6-dichloropyrimidine belong to C_s and C_{2v} point group respectively. In the former case, the molecular plane containing all the atoms will be the only symmetry element and the transition $^1B_1$–$^1A_1$ reduces to an allowed A'–A' transition with the transition moment lying in the plane of the molecule while in the latter case, the molecule will have the same symmetry as that of pyrimidine and the bands will appear due to $^1B_1$–$^1A_1$ transition with the transition moment lying in the plane perpendicular to the para axis passing through 2 and 5 position in the conventional model of pyrimidine (1969) The strongest band appearing at 33121 and 34788 cm^{-1}, on the longer wavelength side of the spectrum, has been taken as the 0, 0 band in the two molecules respectively. In the spectrum of 2,4-dichloropyrimidine, prominent bands positioned at 33555, 33691, 33812, 33922, 34240 and 34604 cm^{-1} involve a separation of 434, 570, 691, 801, 1119 and 1483 cm^{-1} from the 0, 0 band These separations have been taken to represent the excited state fundamental vibrational frequencies

Table 3 A correlation of infrared and ultraviolet absorption frequencies of 2,4- dichloropyrimidine and their assignment to probable mode (All values are in cm^{-1})

IR absorption	UV absorption		Modes of vibration
	G.S.	E.S.	
450	441	—	ν_{16b}
475	—	434	ν_6
615	—	570	
867	—	801	ν_1
1338	—	1119	ν_3
1555	—	1483	ν_{8a}

In the spectrum of 4,6- dichloropyrimidine strong bands at 34969, 35069, 35246, 35482 and 35945 cm^{-1} towards the shorter wavelength side of the 0, 0 band gives excited state fundamentals 181, 281, 458, 694 and 1157 cm^{-1} The hot bands at 34618, 34396, 34262, 34085 and 33921 cm^{-1} on the longer wavelength side of the 0, 0 band in 4,6- dichloropyrimidine involves ground state vibration 170, 392, 526, 703 and 867 cm^{-1} In case of 2,4- dichloropyrimidine one such vibration has been observed at 441 cm^{-1} A correlation of these vibrations along with infrared frequencies are reported in tables 3 and 4. Some of the important modes are discussed.

Table 4 A correlation of infrared and ultraviolet absorption frequencies of 4,6- dichloropyrimidine and their assignment to probable mode
(All values are in cm^{-1})

IR absorption	UV absorption		Modes of vibration
	G.S	E S.	
395	392	--	ν_{10a}
530	526	281	ν_6
620	-	458	
872	867	694	ν_1
1324	--	1157	ν_3

i) ν_1 *Vibration*

In the spectrum of benzene the ν_1 vibration (995 cm^{-1}) represents the C–C stretching (ring breathing) vibration In the spectra of substituted benzenes this vibration has been found to be mass dependent and it has been identified, in the UV, IR and Raman spectra upto 700 cm^{-1} depending upon the mass and nature of the substituent In the UV absorption spectrum of pyrimidine, a medium band towards the longer wavelength, at a separation of 991 cm^{-1} from the 0, 0 band has been assigned as the ν_1 vibration by Simmons & Innes (1964) This assignment is in agreement with the assignment proposed by Lord (1957) from Raman and by Sbrana *et al* (1966) from infrared studies In the vibrational spectrum of pyrimidine-d_4, the same vibration has been assigned at 830 cm^{-1} by Sbrana *et al* (1966) Therefore, from the vibrational studies of pyrimidine-d_4 it appears that ν_1 vibration is dependent on the mass of the substituent It the electronic spectrum of 2,4- and 4,6- dichloropyrimidine, strong bands at 33922 and 35482 cm^{-1} towards the shorter wavelength side of the 0, 0 band involve excited state fundamental having values of 801 and 694 cm^{-1} respectively The 801 cm^{-1} vibration has been traced up to two quanta This vibration has been found in combination with other fundamentals of the same electronic state. In the case of 4,6- dichloropyrimidine the spectrum does not extend much towards the shorter wavelength hence the higher quanta of 694 cm^{-1} vibration has not been traced The ground state value for 801 cm^{-1} has not been observed since the spectrum does not extend much towards the longer wavelength. However, a very strong IR band at 867 cm^{-1} may correspond to it. The ground state value for 694 cm^{-1} has been observed at 867 cm^{-1} which agrees well with the strong IR band observed at 872 cm^{-1}. These two (801 and 694 cm^{-1}) vibrations in the two molecules have been assigned to ν_1 vibration.

(ii) ν_6 *Vibration*

The doubly degenerate ν_6 vibration, having e_{2g} symmetry will split into its components under the reduced C_s and C_{2v} point group. In case of C_s symmetry both the components will be of totally symmetric character whereas in C_{2v} symmetry the lower component will be totally symmetric and the higher component will be non-totally symmetric and therefore will not appear in the electronic spectrum

In the spectrum of 2,4- dichloropyrimidine the bands at $33555 = 0,0+434$ and $33691 = 0,0+570$ cm^{-1} give two excited state fundamental vibration Corresponding to these vibrations no ground state fundamental has been observed. However, the pair of strong infrared vibrations at 475 and 615 cm^{-1} can correspond to the two excited state vibrations respectively.

Two bands at 35069 and 35246 cm^{-1} in case of 4,6- dichloropyrimidine give two 281 and 458 cm^{-1} excited state vibration The combinations formed by these vibrations have also been observed. The ground state value of 281 cm^{-1} is probably 526 cm^{-1} (appearing up to two quanta) which agrees well with the infrared band at 530 cm^{-1} The counterpart of 458 cm^{-1} has not been identified in the electronic spectrum because of its weak intensity However, a weak infrared band at 620 cm^{-1} may correspond to it. These vibrations, in each case, may be assigned as the components of ν_6 vibration

Other excited state vibrations which appear under the similar conditions are 1119 and 1157 cm^{-1} respectively. Infrared bands at 1338 and 1324 cm^{-1} in the two molecules respectively may be due to the two vibrations These vibrations may be assigned as ν_3 (C–H planar bending) vibration

The 0,0 band of the 3200Å system of pyrimidine appears at 31072 cm^{-1} A hypsochromic shift by 2049 cm^{-1} in 2,4- and by 3716 cm^{-1} in 4,6- dichloropyrimidine has been observed The order of the shift is 4,6- > 2,4-

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