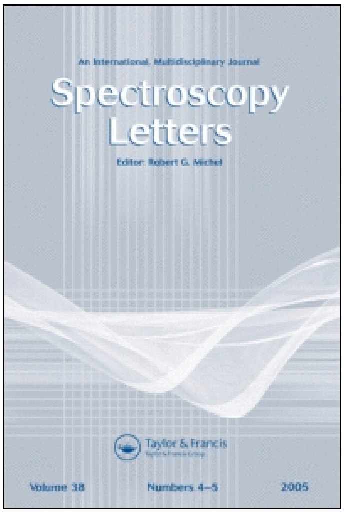

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RAMAN SPECTRUM OF CRYSTALLINE PYRIMIDINE

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In an earlier work[1] we have investigated an oriented crystal of pyrimidine at liquid nitrogen temperature using polarized infrared radiation. The static field effect for an A_2 mode (16a) and correlation field splitting for fourteen fundamentals have been observed[1]. This paper reports the Raman spectrum of crystalline pyrimidine at liquid nitrogen temperature.

The pyrimidine molecule has C_{2v} symmetry. The crystal space group is $Pna2_1(C_{2v}^9)$ with four molecules in the unit cell[2]. There are thus 96 internal vibrations, $24A_1 + 24A_2 + 24B_1 + 24B_2$, and since there is no site symmetry for pyrimidine molecules, we expect each intramolecular mode to be split into four components three of them infrared active and all four Raman active. The external modes, on the other hand, can be represented by $5A_1 + 6A_2 + 5B_1 + 5B_2$, fifteen infrared and twenty one Raman active.

EXPERIMENTAL

The commercial sample purified by repeated sublimations before use was vaporized and the vapors condensed on a cold metal surface oriented at 45° to the incident laser beam. The operation was carried out in vacuum using a Coderg Cryocirc cryostat. The Raman spectra of polycrystalline pyrimidine were examined at 153° and 90°K. Spectral slitwidths of 1 cm^{-1} were used for strong bands and 2, 4, and 8 cm^{-1} for weaker bands. The positions of the bands are probably good to $\pm$ 1 cm^{-1}. The intensities were not corrected. The instrument in this study was a Coderg Raman Model PH1 spectrograph equipped with a double monochromator. The sample was excited by the 6328 Å line of a Spectra-Physics Model 125 He-Ne laser.

RESULTS AND DISCUSSION

The Raman spectrum of crystalline pyrimidine, at 90°K, 3100-3000, 1600-300, and 120-35 cm^{-1} regions, is shown in Fig. 1. The spectrum recorded at 153°K is similar, however, practically no splitting of the fundamentals has been observed at that temperature. The Raman frequencies are compared to the infrared ones in Tables 1 and 2. Intensities of the Raman lines are in arbitrary units with respect to the strongest 994 cm^{-1} line to which the intensity of 100 is given.

Intramolecular Vibrations

The splitting of the bands does not appear to be due exclusively to the correlation field of the crystal and is occasionaly caused by combinations and overtones, particularly in the region above 1000 cm^{-1}. The intensity of the combination bands may sometimes be enhanced by Fermi resonance which complicates the interpretation of the spectrum. In the following, the 3100-3000, 1600-1300, 1300-900, and 900-200 cm^{-1} spectral regions will be discussed successively, in order to check the conclusions drawn from our infrared data[1]. The assignment of the intramolecular fundamentals is given in terms of C_{2v} symmetry of an isolated molecule following the notation of Lord et al.[3].

In the 3100-3000 cm^{-1} region, where four CH stretching fundamentals are expected, eight Raman and infrared bands are observed at similar frequencies. No measurable correlation splitting of the νCH fundamentals could be shown by infrared dichroism measurements[1]. There are thus four

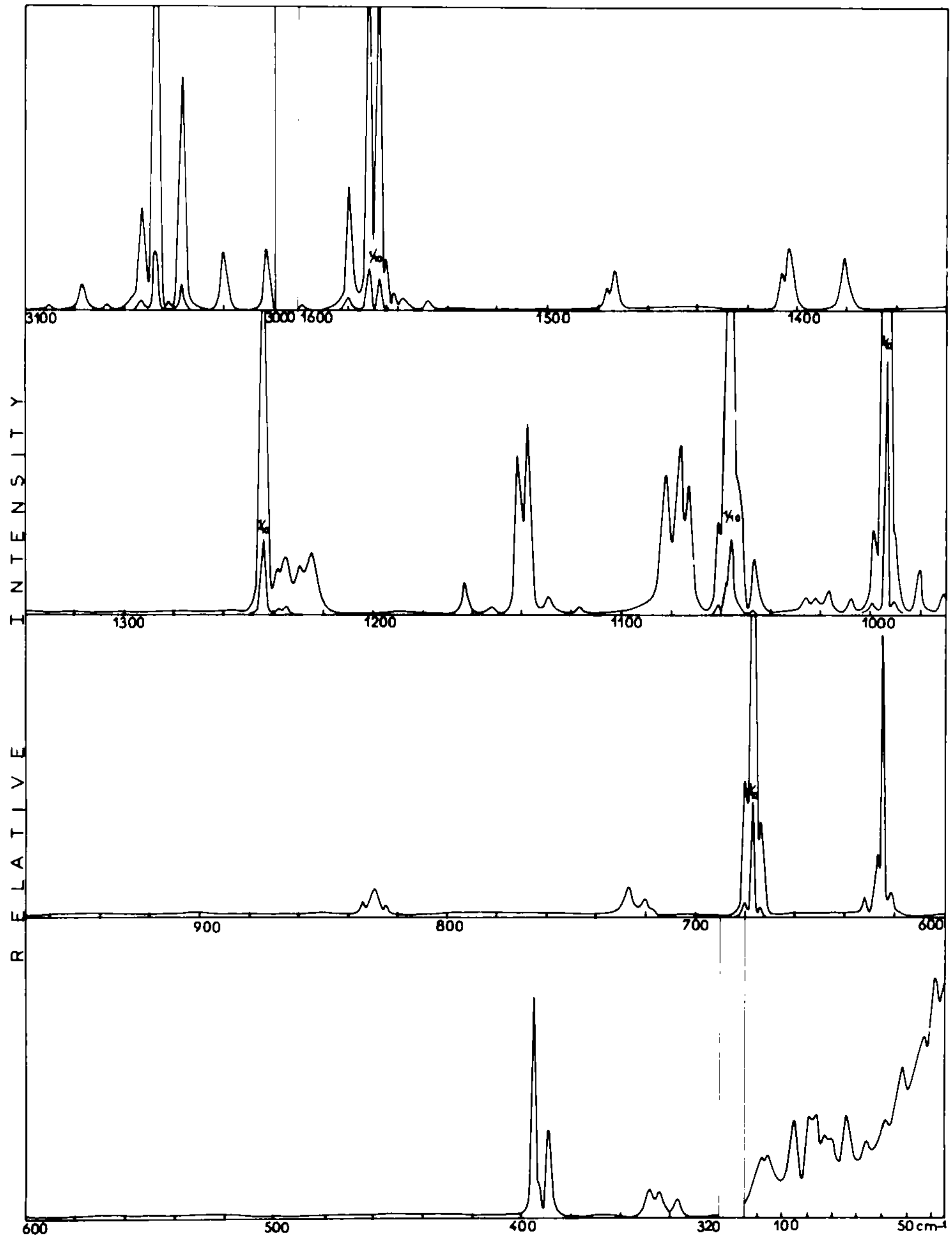

Figure 1

Raman spectra of Crystalline Pyrimidine at 90°K

TABLE 1

Infrared and Raman frequencies of Crystalline Pyrimidine at 90°K

IR	Raman	Assignment
3090 w	3092 (0)	comb
3077 m	3079 (1)	7b (B_1)
3069 sh	3069 (0)	comb
3055 w	3055 (4)	comb
3049 m	3050 (22)	2 (A_1)
3039 w	3039 (9)	20a (A_1)
3022 w	3022 (2)	comb
3004 m	3005 (2)	13 (A_1)
1577 vs	1581 (5)	8a (A_1)
1570 vs	1573 (17)	
1568 vs	1569 (13)	8b (B_1)
1563 m	1566 (2)	
1558 sh	1559 (0)	comb
1550 m	1549 (0)	
1479 m		19b (B_1)
1475 m	1477 (1)	
1473 sh	1474 (2)	
1463 m		
1402 vs	1407 (2)	19a (A_1)
1398 sh	1404 (3)	
1392 m		
1382 m	1382 (2)	14 (B_1)
1380 m		
1372 sh		
	1244 (28)	3 (B_1)
1238 m	1238 sh	
1233 w	1235 (2)	
	1229 sh	
1224 sh	1225 (2)	
1162 m	1163 (1)	15 (B_1)
1155 w	1153 (0)	comb
1143 m		9a (A_1)
1141 m	1142 (7)	
1138 m	1138 (6)	
1136 sh		comb
1126 vw	1129 (1)	
1113 vw	1117 (0)	
1086 m	1082 (6)	
1080 m	1076 (7)	
1075 w	1073 (5)	
	1066 sh	12 (A_1)
1060 w	1056 (29)	
	1054 sh	
	1047 (2)	
1027 sh	1026 (1)	18b (B_1)
1024 w	1022 (1)	
1018 vw	1017 (1)	
	1008 (1)	comb
992 ms	994 (100)	1 (A_1)
989 ms	991 (3)	
999 m	999 (3)	5 (B_2)
980 m	981 (2)	
970 w	971 (1)	
	834 (1/2)	10b (B_2)
835 s	829 (1)	
825 s	825 (1/2)	
726 vs	727 (1)	
720 vs	720 (1/2)	11 (B_2)
717 sh	717 sh	4 (B_2)
679 m	680 (5)	6a (A_1)
673 m	677 (16)	
668 w	674 (4)	
631 s	632 (1)	6b (B_1)
628 s	627 (3)	
625 sh	621 (11)	
621 m	622 (1)	
396 w	395 (9)	16a (A_2)
394 w	393 sh	
390 w	389 (3)	
	348 (1)	16b (B_2)
342 m	344 (1)	
	337 (1)	

νCH and four combination bands in this region. The identification of the νCH frequencies at 3050, 3079 and 3005 cm^{-1} appears straightforward, the first being very strong in Raman and the others relatively strong in infrared. The fourth νCH fundamental can be either of the intense 3039 and 3055 cm^{-1} Raman lines, which implies that one of them is probably a combination band in Fermi resonance with the 3050 cm^{-1} fundamental.

There are five predominantly skeletal vibrations between 1600 and 1300 cm^{-1}. The assignment of two doublets, 1581, 1573 and 1569, 1566 cm^{-1}, to the ν8a and ν8b fundamentals, respectively, is consistent with the infrared dichroism and Raman intensities. The 1559 and 1549 cm^{-1} bands, very weak in the Raman spectrum, must be due to combinations. Doublets are also observed for the ν19a and ν19b modes. The assignment of the ν14 fundamental[1] to an infrared 1382, 1380 cm^{-1} doublet is supported by the 1382 cm^{-1} Raman band ; the interpretation of Lord et al.[3] appears thus preferable to that of Califano et al.[4].

1200-900 cm^{-1} region. Five Raman peaks are observed between 1250 and 1220 cm^{-1} where the ν3 vibration is expected. The 1244 and 1238 cm^{-1} frequencies are very likely to be fundamental, appearing as strong bands in Raman and infrared respectively. Among the remaining three components, at least one has to be considered as a combination. The ν15 mode gives a singlet at 1162 cm^{-1} whereas a strong doublet, 1142, 1138 cm^{-1}, is observed for the ν9a vibration. Two groups of strong Raman bands near 1076 and 1056 cm^{-1} pose a problem. If the interpretation proposed by Lord et al.[3] for the 1053-1074 cm^{-1} Raman doublet of the liquid pyrimidine as due to Fermi resonance of the ν12 fundamental with the ν16b + ν11 combination is extended to the crystal, it must be assumed that each of the three components at 1082, 1076 and 1073 cm^{-1} undergoes a similar effect. A relatively weak Raman triplet, 1026, 1022 and 1017 cm^{-1}, has its infrared counterpart and is assigned to the ν18b mode. In the 1000-970 cm^{-1} range, five Raman bands at 999, 994, 991, 981 and 971 cm^{-1} belong to the ν1(A_1) and ν5(B_2) vibrations. Combined results of the infrared dichroïsm[1] and Raman intensities, permit one to assign the 994 and 991 cm^{-1} components to the ν1 and those at 999, 981 and 971 cm^{-1} to the ν5 modes.

900-200 cm^{-1} region. Triplets are observed for ν10b, ν6a, ν16a, and ν16b and a quartet for the ν 6b vibrations. In each case, the splitting is believed to be due the correlation effect of the crystal. The triplet 727, 720 and 717 cm^{-1}, on the other hand, could be due to both ν11 and ν4 vibrations of the B_2 species. The assignment of very strong Raman lines near 677 and 621 cm^{-1} to ν6a and ν6b modes respectively agrees with that of Califano et al.[4] and disagrees with that of Lord et al.[3] who reported a Raman band near 567 cm^{-1}, assigned to the ν6a fundamental of the liquid pyrimidine ; we could not observe any band in the 600-400 cm^{-1} region of the Raman and infrared spectra of the crystal. The 870 cm^{-1} Raman band assigned to the ν17a vibration (A_2) of the liquid[3] does not appear either in the crystal spectra.

Twenty two intramolecular fundamentals have thus been observed in the Raman spectrum of pyrimidine crystal. One of the remaining two, the ν17a mode, has not been identified and the second (ν4) cannot be distinguished from ν11 or vice-versa. Four components, which may be due to the crystal effect, show up for ν6b, ν12 and ν3 modes, whereas νCH and ν15 vibrations give singlets. The other fundamentals appear as doublets or triplets.

Lattice Vibrations

There are 12 rotational and 9 translational vibrations of pyrimidine crystal expected to be Raman active. In the observed spectrum of this compound at 90°K, 13 bands are found in the 120-35 cm^{-1} range (Fig. 1, Table 2) and all are due to lattice modes since the lowest intramolecular frequency is identified at 337 cm^{-1}. Thus, the Raman spectrum appears much richer than the infrared spectrum, since, for the latter only three absorption bands have been observed (Table 2). The lattice frequencies occur in the same spectral region as those of pyrazine[5] but no assignment has been attempted for the present.

TABLE 2

Raman and Infrared frequencies of lattice vibrations of crystalline pyrimidine

Raman (153°K)	106 m 103 sh	95 s	86 s 80 sh	72 s	65 w	56 sh 51 m	42 sh 39 s
Raman (90°K)	108 m 106 m	95 s	89 s 86 s 83 m 80 sh	74 s	66 w	58 sh 52 m	43 m 39 s
Infrared (90°K)	106 m	97 m		72 m			

REFERENCES

1. R. Foglizzo and A. Novak, J. Chim. Phys., 64, 1484 (1967)

2. P. J. Wheatley, Acta Cryst., 13, 80 (1960)

3. R. C. Lord, A. L. Marston, and F. A. Miller, Spectrochim. Acta, 9, 113 (1957)

4. G. Sbrana, G. Adembri, and S. Califano, Spectrochim. Acta, 22, 1831(1966)

5. M. Ito and T. Shigoeka, J. Chem. Phys., 44, 1001 (1966)

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