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Laser Raman and Infrared Spectroscopic Studies on 5-Methyl Cytosine

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The laser Raman and infrared spectra of 5-methyl cytosine have been recorded on a Cary model 82 grating spectrophotometer with an argon laser source and Perkin-Elmer 983 double beam grating spectrophotometer respectively. The spectra have been analysed on the basis of fundamentals, combinations and overtones and the frequencies have been assigned to various modes of vibration assuming C_s point group symmetry. Further based on the present assignment, a complete vibrational analysis has been carried out for this molecule and the results are briefly discussed.

INTRODUCTION

N-Heterocyclic molecules such as cytosine and their derivatives are of great biological significance. But very little spectroscopic information is available for these molecules in the literature. This is due to the difficulty in interpreting the spectra of this type of complex molecule with low symmetry. The study of the vibrational spectra is important to get information on their molecular confirmation and hydrogen bonding.

EXPERIMENTAL

The laser Raman spectrum of 5-methyl cytosine was recorded using 488 nm line of Ar^+ for excitation in the region 100–4000 cm^{-1} in a Cary Model 82 grating spectrophotometer and using a 4W argon laser. The infrared spectrum of the sample was also recorded on a Perkin Elmer 983 double beam grating spectrophotometer in the region 200–4000 cm^{-1}. The frequencies for all sharp bands are accurate to ± 1 cm^{-1}.

The structural parameters for this molecule are assumed from the allied molecules. The normal coordinate calculations were performed using the program due to Schachtschreider[1]. The valence force field was adopted for both in-plane and out-of-plane vibrations.

RESULTS AND DISCUSSION

The observed frequencies of 5-methyl cytosine along with relative intensities and possible assignments are presented in Table 1. Taking into account of normal coordinate calculations, group frequency approach and the analogy between the spectra of molecules of similar structure, the observed bands have been assigned in terms of fundamentals, combinations and overtones. Since all the fundamentals are active in both infrared and Raman, the present study aims to assign all the vibrational fundamentals of this molecule.

Assuming the molecule 5-methyl cytosine to have C_s point group and considering NH_2 and CH_3 groups as point masses all the assignments have been made.

C_s symmetry leads to two types of vibrations distributed as

$$\Gamma = 21a' \text{ (planar)} + 9a'' \text{(non-planar)}$$

in which a′ gives rise to polarised lines whereas a″ gives depolarised lines in Raman spectrum. The vibrations are divided into (i) Phenyl ring vibrations, and (ii) NH_2 and CH_3 group vibrations.

(i) Phenyl Ring Vibrations

(a) Carbon Vibrations: Benzene has two doubly degenerate modes e_{2g} (1596 cm^{-1}) and e_{1u} (1585 cm^{-1}) and two non-degenerate modes b_{2u} (1310 cm^{-1}) and a_{1g} (995 cm^{-1}) due to skelton stretching modes of C—C bonds. The very strong polarized bands observed at 1481 cm^{-1} & 1395 cm^{-1} in 5 methyl cytosine bands observed at 1481 cm^{-1} & 1395 cm^{-1} in 5-methyl cytosine are assigned to C—C stretching vibrations.

The carbon out of plane bending vibrations are derived from the non-degenerate b_{2g} (703 cm^{-1}) and degenerate e_{2u} (404 cm^{-1}) modes of benzene. In the present case the band observed at 441 cm^{-1} and 350 cm^{-1} are assigned to carbon out-of-plane bending vibrations in 5-methyl cytosine. The C—C ring breating a_{1g} (995 cm^{-1}) and C—C—C trigonal bending, non-degenerate b_{1u} (1010 cm^{-1}) vibrations of benzene. Under C_s symmetry give rise to combined modified modes. In substituted benzene, one mode comes to about 800 cm^{-1} while the other appears at 1000 cm^{-1}. In the present case C—C ring breathing vibrations have been assigned to 768 cm^{-1} in 5-methyl cytosine. The carbon ring deformation frequencies arise due to the degenerate vibration e_{2g} (608 cm^{-1}) of benzene. It has been noticed in many cases that one component depends upon the disposition as well to the mass of the substituent and reduces much. In the present work the band at 605 cm^{-1} has been assigned to the component of e_{2g} (608 cm^{-1}) mode of benznne.e

(b) C—H Vibrations: The aromatic structure shows the presence of C—H stretching vibrations in the region, 3000–3100 cm^{-1} which afford a ready

TABLE 1: ASSIGNMENT OF FUNDAMENTAL INFRARED AND LASER RAMAN FREQUENCIES (cm^{-1}) OF 5-METHYL CYTOSINE

Species	Infrared		Laser Raman		Description of assignment and PED%
	Frequency	Relative intensity	Frequency	Relative intensity	
a′	3418	VS	3412	VS	NH_2 asym. stretching (88)
a′	3320	M	3309	S	NH_2 sym. stretching (90)
a′	3141	S	3141	M	N—H stretching (95)
a′	3027	M	3021	M	CH aromatic stretching (96)
a′	2962	M			CH aliphatic asym. stretching (91)
a′	2850	M	2851	M	CN aliphatic sym. stretching (83)
	2462	(2 × 1230)			
	1952	(1450 + 502)			
a′	1604	W	1610	W	NH_2 in-plane deform (75)
a′	1593	W	1597	W	NH_2 in-plane deform (71)
a′	1486	W	1481	S	C—C stretching (83)
a′	1450	VS	1451	M	CH_3 sym. deform (79)
a′	1396	VS	1395	VS	C—C stretching (94)
a′	1380	W	1386	W	CH_3 sym. deform (91)
a′	1342	S	1341	S	C—H in-plane bending (90)
	1298	W	1295	VS	C—NH_2 stretching (79)
a′	1290	M	1291	W	C—N stretching (90)
a′	1230	S	1229	W	C—O stretching (86)
a′	1200	VS	1201	S	C—CH_3 stretching (65)
a′	1128	S	1131	S	NH_2 rocking (66)
a′	1053	W			NH_2 twisting (76)
	972	M	970	W	(C—NH_2) in-plane bending (76)
a″	875	W	881	W	NH nonplanar vibs (69)
a″	801	S	802	S	NH non-planar deform (66)
a″	796	M			C—H out-of-plane bending (89)
a′			768	S	C—C ring breathing (83)
a″	674	W	671	M	NH_2 out-of-plane wagging (81)
a′	605	M			(C—C—C) in-plane bending (79)
a′	570	M	571	M	C=O in-plane bending (60)
a′					C—N in-plane bending (40)
a″	502	W			NH_2 out-of-plane bending (65)
a″			441	W	(C—C—C) out-of-plane bending (74)
a″	401	W	401	M	(C=O) out-of-plane bending (56)
a″					(C—N) out-of-plane bending (44)
	380	M	381	W	(C—CH_3) in-plane bending (78)
a″			350	M	(C—C—C) out-of-plane bending (62)

identification for this structure. The Raman band at 3021 cm^{-1} is assigned to C—H stretching mode. These observations are in good agreement with the literature values[2,3].

The medium band at 796 cm^{-1} is assigned to C—H out-of-plane vibration.

(c) **N—H, C—N and C—O vibration:** The medium intensity band in laser Raman spectrum at 3141 cm^{-1} is assigned to N—H stretching vibration. As expected the bands at 1291 and 1229 cm^{-1} are assigned to C—N and C—O stretching vibrations respectively[4].

(ii) NH_2 and CH_3 Group vibrations

In the spectra of 5-methyl cytosine the strong bands at 3412 and 3309 cm^{-1} are assigned to NH_2 asymmetric and symmetric stretching vibrations. Similarly C—H asymmetric and symmetric stretching vibrations, in methyl groups are assigned to 2962 and 2850 cm^{-1} respectively. These observations are in good agreement with Fox and Martin[5].

In nearly all the primary aromatic amines a strong band occurs in the region 1250–1340 cm^{-1} and it is identified as C—NH_2 vibration[6]. On this basis, a very strong band occuring at 1295 cm^{-1} is assigned to C—NH_2 stretching vibration in 5-methyl cytosine. The strong band which appears at 1200 cm^{-1} in substituted toluenes[7] is identified as a C—CH_3 stretching vibration. In line with the above observation, the band at 1201 cm^{-1} in the spectra of 5-methyl cytosine is assigned to C—CH_3 stretching vibration.

In many substituted toluidines, the NH_2 twisting vibration is observed around 1060 cm^{-1}. On this basis, the weak band at 1053 cm^{-1} in the infrered spectrum is assigned to the NH_2 twisting vibration in 5-methyl cytosine. Further it may also be noted that NH stretching vibration in the group appear very strong when compared to NH ring vibrations.

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