

## Vibrational spectral study of 2-Chloro-6-methoxy pyridine

B.S. YADAV\*, RITU SHARMA and ISRAT ALI

Molecular Spectroscopy and Biophysics Laboratory, D.N. College, Meerut - 250 002 (India)

(Received: March 15, 2007; Accepted: May 02, 2007)

### ABSTRACT

The FTIR and Laser Raman spectra of 2-Chloro-6-methoxy pyridine have been recorded in the region  $4000-400\text{ cm}^{-1}$  and  $4000-100\text{ cm}^{-1}$  respectively. The bands observed in the FTIR spectra and Laser Raman spectra are discussed by assuming the compound under  $C_s$  point group symmetry. The probable assignments of the above molecule are based on group frequency approach together with the data available for similar molecules.

**Key words:** FTIR spectra, Laser Raman spectra, 2-Chloro-6-methoxy pyridine.

### INTRODUCTION

The spectroscopic study of N-heterocyclic molecules including substituted pyridines have become quite interesting as they are the constituent of DNA and RNA and hence play a central role in the structure and properties of nucleic acids<sup>1-3</sup>. Infrared and Laser Raman spectra of pyridine and its monosubstituted derivatives have been studied by several investigators but a little work appears on the vibrational spectra of di and trisubstituted pyridines<sup>3-5</sup>. The present work has been done to interpret completely the vibrational spectra of 2-chloro-6-methoxy pyridine which has not been reported earlier.

### EXPERIMENTAL

Specpure grade chemical 2-chloro-6-methoxy pyridine was obtained from M/S Aldrich Chemie, West Germany and used as such. This chemical hereafter, referred as 2,6-CMP. The purity of the said molecule was also confirmed by elemental analysis and melting point determination. The FTIR absorption spectra of 2,6 CMP was recorded on Perkin Elmer spectrophotometer model - 52 in the region  $4000-400\text{ cm}^{-1}$  in nujol mull and Laser Raman spectra of the above molecule has been recorded on Spex-Rama Lab spectrophotometer using Argon - Neon Laser Beam of light

of wavelength 488nm and power of 200 mw. All the bands are expected to be accurate  $\pm 7\text{ cm}^{-1}$ .

### RESULTS AND DISCUSSION

The structural formula of the molecule 2,6 - CMP is given in figure 1.

The FTIR spectra in nujol mull and Laser Raman spectra of the said molecule are given in figures 2 and 3 respectively. The fundamental vibrational frequencies of the said molecule are given in Table 1. For simplicity and convenience the modes of vibrations of the aromatic compounds are considered as guidelines.

- Vibrational spectra
- Ring vibrations
- C-H vibrations

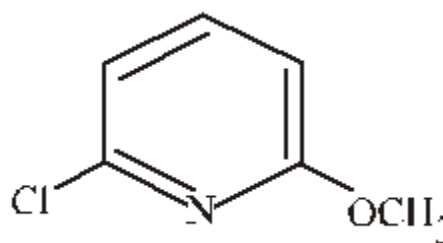


Fig. -1: Molecular structure of 2, 6 - CMP.

**Table -1: Assignments of the vibrational frequencies in (cm<sup>-1</sup>) of 2,6-CMP**

FTIR	Laser Raman	Assignments
–	3146 vw	ν (C-H)
3104vw	–	ν (C-H)
–	3082ms	ν (C-H)
–	3013vw	ν (C-H) Asym (O-CH <sub>3</sub> ) Group
2956vw	2951 ms	ν (C-H) Asym (O-CH <sub>3</sub> ) Group
–	2905 vw	ν (C-H) Sym (O-CH <sub>3</sub> ) Group
–	1641 w	ν Ring
1602s	–	ν Ring
1566s	1568ms	ν Ring
–	1538w	ν Ring
1476s	–	ν (C-N)
1418s	–	ν (C=N)
–	1390w	β (C-H)
1305s	1298ms	β (C-H), ν(C-OCH <sub>3</sub> )
1266w	1265 w	β (C-H) O-CH <sub>3</sub> Group
–	1238w	β (C-H) O-CH <sub>3</sub> Group
1149ms	1148ms	β (C-H)
–	1069ms	CH <sub>3</sub> Wagging
1026 ms	–	CH <sub>3</sub> Rocking
986w	982s	ν (C-Cl)
879ms	–	γ (C-H)
–	862w	γ (C-H)
–	847w	Trigonal Bending
787ms	–	Trigonal Bending
–	766w	Ring Breathing
–	746 w	C-N-C Bending Vibration
731 vw	–	β(C-OCH <sub>3</sub> )
690 vw	–	γ (C-H)
–	678 ms	β Ring
–	629 w	β Ring
609 vw	605 ms	β Ring
–	522w	β (C-Cl)
–	467ms	γ Ring
416vw	410 ms	γ Ring
–	278 w	γ (C-OCH <sub>3</sub> )
–	185 ms	γ (C-Cl)

ν = Stretching, β = In-plane bending,

γ = Out-of-plane bending, Sym =Symmetric,

Asym = Asymmetric

w = Weak, vw = Very weak, ms = Medium strong, s = Strong

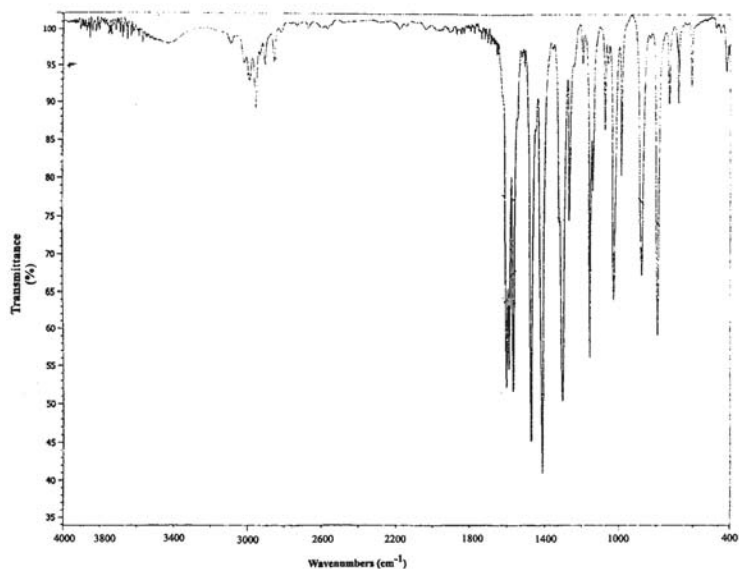


Fig. - 2: FTIR spectrum of 2,6 - CMP

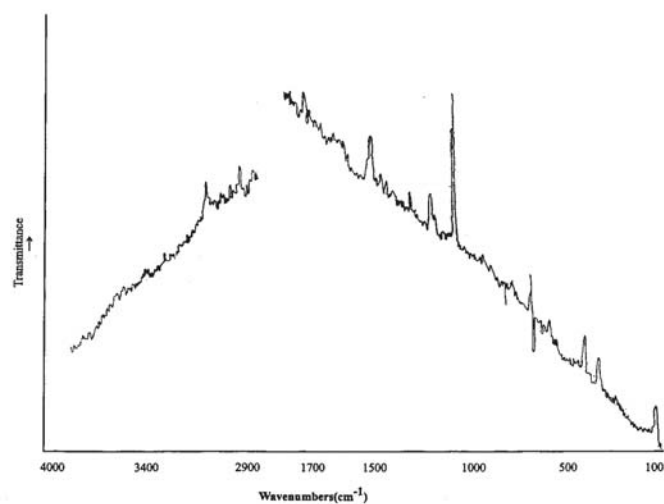


Fig. - 3: Laser raman spectrum of 2,6 - CMP

Since the molecule 2,6-CMP is a disubstituted pyridine, it has 3 hydrogen atoms left around the ring. Thus the molecule 2, 6 - CMP may have three C-H valence oscillations which usually lie in the region  $3150-3000\text{ cm}^{-1}$ .<sup>5-7</sup> Thus the two bands observed at  $3146, 3082\text{ cm}^{-1}$  in Raman and one band observed at  $3104\text{ cm}^{-1}$  in IR have been assigned to the C-H ring stretching vibrations of the above molecule. These assignments are also in good agreement with the literature value<sup>6-8</sup>. Yadav *et al.*<sup>4</sup> have assigned in-plane bending vibration at

$1294\text{ cm}^{-1}$  in 2- phenyl pyridine and at  $1280\text{ cm}^{-1}$  in 4-phenyl pyridine and out-of-plane bending in the region  $750-980\text{ cm}^{-1}$  in 2 and 4-phenyl pyridine. In view of these the bands observed in IR at  $1305\text{ cm}^{-1}$  and its counterpart in Raman at  $1298\text{ cm}^{-1}$  has been taken to represent C-H in-plane ring bending vibration. One band also observed at  $1390\text{ cm}^{-1}$  having weak intensity also represent C-H in-plane bending vibration. The two bands one in IR at  $879\text{ cm}^{-1}$  and other in Raman at  $862\text{ cm}^{-1}$  have been assigned to out-of-plane bending vibrations. These

assignments find support with the literature value<sup>9-11</sup>.

### C–N and C–C vibrations

In benzene and substituted benzene the frequency of ring breathing mode have been assigned in the region 844-690  $\text{cm}^{-1}$ . Yadav et al<sup>4</sup>, have assigned ring breathing mode at 782  $\text{cm}^{-1}$  in 5-chloro 2,3 -dihydroxy pyridine. In view of this a weak band observed at 766  $\text{cm}^{-1}$  in Laser Raman spectra of the above molecule has been assigned to ring breathing mode of vibration. The C-C and C-N stretching in-plane and out-of-plane bending modes have been assigned in their respective regions<sup>4-7</sup> which are given in Table 1. The trigonal bending and C-N-C bending vibrations have been assigned at 787  $\text{cm}^{-1}$  and 746  $\text{cm}^{-1}$  in FTIR and Laser Raman spectra respectively. These assignments agree well with the work of other investigators on similar molecules<sup>11-12</sup>.

### C-X vibrations

The C-Cl stretching frequencies generally observed near the region 1000  $\text{cm}^{-1}$ . Based on this the bands at 986  $\text{cm}^{-1}$  of weak intensity in FTIR and its counterpart at 982  $\text{cm}^{-1}$  of strong intensity in Laser Raman spectra of the above molecule has

been taken to represent C-Cl stretching vibration.

The in-plane C-Cl bending vibration has been assigned at 522  $\text{cm}^{-1}$  in Laser Raman spectra and the out-of-plane bending vibration has been observed at 185  $\text{cm}^{-1}$  in Laser Raman spectra of this molecule with medium strong intensity. The assignments are in good agreement with the earlier workers<sup>7-10</sup>. The methoxy group present at the 6<sup>th</sup> position in 2,6-CMP give rise to stretching as well as in-plane and out-of-plane bending vibrations which are observed at 1298, 731 and 278  $\text{cm}^{-1}$  for the above compound. The assignments fairly agree with the literature values<sup>6-9</sup>.

### Group vibrations

#### OCH<sub>3</sub> group

The methoxy group at 6<sup>th</sup> position in the ring system gives internal vibrations<sup>5-8</sup>. Two antisymmetric and one symmetric C-H stretching vibrations have been found in O-CH<sub>3</sub> group which are given in Table 1. CH<sub>3</sub> wagging and rocking are also found at 1069 and 1026  $\text{cm}^{-1}$  in Laser Raman & FTIR spectra respectively of the above molecule. These assignments are in good agreement with the literature values<sup>9-12</sup>.

## REFERENCES

1. Yadav B.S., Seema, Kumar Vipin and Jetley U.K. *Indian J. Pure & Appl. Phys.* **35** 587 (1997).
2. Yadav B.S., Singh Vir, Yadav M.K. and Chaudhary S. *Indian J. Phys.* **35** 305 (1997).
3. Yadav B.S., Kumar Vipin, Singh Vir and Semwal B.S. *Indian J. Pure & Appl. Phys.* **37** 34 (1999).
4. Yadav B.S., Kumar Nitin, Singh M.K. and Yadav M.K. *Indian J. Phys.* **80** (1), 61-65 (2006).
5. Krishna kumar V. & Ramasamy R., *Indian J. of Pure & Appl. Phys.* Vol. **41**, 258-261, (2003).
6. Krishna kumar V. & Ramasamy R., *Indian J. Pure & Appl Phys.* **39**, 829, (2001).
7. Ahmad Salik, Sharma S.D., Isaq M. *Spectrochimica Acta Part A* **52**, 1369-1373, (1996).
8. Mohan S. & Ilangoan V. *Indian J. of Pure & Appl. Phys* Vol. **32**, 91-95, (1994).
9. Kumar Parveen and Sharma S.D. *Asian J. of Chem.* Vol. **9**, No. 2, 288-292, (1997).
10. Mohan S. & Murugan R. *Indian J of Pure & Appl. Phys.* Vol. **30**, 283-286, (1992).
11. Isaq M., Gupta S.P., Sharma S.D. and Yadav B.S. *Oriental J of Chem.* Vol. **14**, (3) 387-392, (1998).
12. Isaq M., Gupta S.P., Sharma S.D. and Yadav B.S. *Oriental J of Chem.* Vol. **14**, (3) 417-422, (1998).