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NOTE

Laser Raman and Infrared Spectra of 3-Cyanopyridine

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The Laser Raman and IR spectra of 3-cyanopyridine have been reported along with their assignments. An assignment of fundamentals is proposed and comparison with similar molecules is discussed.

N-Hetereocyclic molecules like pyridine, pyrimidine, cytosine, uracil etc. and their derivatives are of immense importance as they play a central role in the structure and properties of the DNA and RNA. The pyridine ring system is very important as a structural unit in the natural products and compounds of pharmaceutical interest. The vibrational spectra of biologically important pyridines have been analysed previously[1–3]. Difference of absorption depends upon the numbr and position of the substituents. Medhi[4], Goel[5] and Gupta *et al.*[6] have studied the spectra of some substituted pyridines. In continuation of our studies[7], the present work has been done to interpret completely the IR and Raman spectra of 3-cyanopyridine which has not been reported earlier.

Spec-pure compound 3-cyanopyridine has been obtained from M/s Fluka Chemie, Switzerland and used as such without further purification. However, its purity has been confirmed by elemental analysis and melting point determination (m.p. 48–52°C). The IR spectra have been recorded on Perkin-Elmer FTIR spectrometer in the region 4000–400 cm^{-1} using KBr pellets, while Raman spectra have been recorded on Brucker IFS 66V FTIR instrument with FT Raman attachment (FRA 106 Raman Module) in the region 3500–100 cm^{-1}.

Ring fundamentals along with substitution group vibrations are presented in Table-1. Considering the cyano group as a single mass point, the molecule under consideration can be assigned C_{2v} group symmetry under which 30 vibrations of pyridine would appear.

Ring Vibrations

In substituted benzene, the C—H stretching frequency almost retained the frequency of benzene in the region 3100–3000 cm^{-1} while the other three frequencies depends upon the mass and nature of the substituents and decrease considerably to below 1200 cm^{-1}.[8] Since the spectra of pyridine and benzene are similar in vibration so the IR bands at 3439 and 3059 cm^{-1} and Raman bands at

3092 and 3061 cm^{-1} are assigned to C—H stretching vibration which are correlated with various researchers[3, 6, 9]

Further the substituted benzene gives rise to C—H in-plane bending and C—H out-of-plane bending. In the present study, these are assigned at 1185 and 700 cm^{-1} in IR mode. The band at 1189 cm^{-1} in Raman spectra is assigned to C—H in-plane-bending. These are in good agreement with literature values[9].

TABLE-1

ASSIGNMENTS OF VIBRATIONAL FREQUENCIES (cm^{-1}) of 3-CYANOPYRIDINE

Infrared Freq.	Raman Freq.	Assignments	
3439 b	—	ν(C—H)	aromatic stretch
—	3092 mw	ν(C—H)	aromatic stretch
3059 s	3061 s	ν(C—H)	aromatic stretch
2365 m	—	—	—
2229 vs	2232 vvs	ν(C—CN)	stretching
1720 m	—	ν(C—C)	ring stretching
1638 m	—	ν(C—C)	ring stretching
1586 s	1588 s	ν(C—C)	ring stretching
1563 ms	1564 vvw	ν(C—C)	ring stretching
1471 vs	1474 vvw	ν(C—C, CN)	ring stretching
1418 vs	1422 vw	ν(C—C, CN)	ring stretching
1210 ms	1210 sh	β(C—H)	in-plane bending
1185 ms	1189 ms	β(C—H)	in-plane bending
—	1063 vvw	β(C—H)	in-plane bending
—	1035 s	β(C—H)	in-plane bending
1023 vs	1023 ms	β(C—N)	in-plane bending
974 m	—	ν(C—C)	stretch-breathing type
810 vvs	—	C—C—C	trigonal bending
779 mw	780 ms	C—C—C	trigonal bending
700 vvs	—	γ(C—H)	out-ot-plane bending
610 vs	631 mw	γ(C—C)	out-ot-plane bending
554 s	554 w	β(C—C)	in-plane bending
471 ms	473 mw	γ(C—C)	out-of-plane bending
	396 mw	γ(C—C)	out-ot-plane bending
	176 s	β(C—CN)	in-plane bending

s—strong, vs—very strong, vvs—very very strong, ms—medium strong, w—weak, vw—very weak, vvw—very very weak, m—medium, b—broad, sh—shoulder.

Hussain *et al.*[10] assigned ring breathing mode at 994 cm^{-1} in 2-chloropyridine. Recently Salik *et al.*[11] assigned this frequency at 820 cm^{-1} in substituted pyrimidines. Considering these facts a medium band has been assigned to this mode at 974 cm^{-1} in IR spectra of 3-cyanopyridine. No such mode is obtained in Raman spectra.

Silverstein[12] assigned C—N stretching absorption in the region 1342–1266 cm^{-1} for aromatic amines. In the present work, the bands observed at 1471 cm^{-1} in the IR spectra and at 1474 cm^{-1} in Raman spectra have been assigned to the C—N stretching vibration and are correlated with literature values[13].

C—CN vibration

According to Bellamy[8], the C—CN stretching vibrations for arylnitrile appear between 2240–2220 cm^{-1} in the IR spectra. Recently Medhi *et al.*[4] gave C—CN strecting vibration for 4-cyanopyridine at 2240 cm^{-1} in IR spectra and 2237 cm^{-1} in Raman spctra. In the present study we have assigned this frequency at 2229 cm^{-1} in IR and at 2230 cm^{-1} in Raman spectra.

All the other ring vibrations are well assigned and are given in Table-1.

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