

FTIR and laser Raman spectra of 2-hydroxy-5 - methyl-3-nitro pyridine

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The FTIR and laser Raman spectra of 2-hydroxy-5-methyl-3-nitro pyridine have been recorded in the region 4000-400cm⁻¹ and 4000-50cm⁻¹, respectively. Both the spectra have been analyzed on the basis of Cs point group symmetry and the observed bands have been assigned to the different specific modes of vibrations. The assignments of FTIR and laser Raman bands of said molecule are made on the basis of magnitude and relative intensities of the observed bands. The assignments made for the complex molecule under investigation are in good agreement with the earlier work on some pyridine derivatives.

Keywords: FTIR, Laser Raman spectra, 2-hydroxy-5-methyl-3-nitro pyridine, Vibrational assignments

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1 Introduction

The spectroscopic study of N-heterocyclic molecules including substituted pyridines, pyrimidines has become quite interesting as they are the constituents of DNA and RNA and hence, play a central role in the structure and properties of the nucleic acids. The pyridine ring system is also very important as a structural unit in the natural products and compounds of pharmaceutical interest¹⁻⁵. The spectroscopic study of these compounds has been motivated for its use to understand the specific biological process and in the analysis of relatively complex system⁶⁻¹⁰. In pyridine system, a large amount of intermolecular association is possible because of its greater polarity. The nitrogen atom is located in sp²-hybridized orbital, which is perpendicular to π -system of the ring. A consequence of this structural feature is that the lone pair of electron and nitrogen atom is not associated with the ring and is available for protonation. The basicity becomes more pronounced if electron-donating groups are present on the ring at second and sixth position, because they alter the electron availability on the nitrogen atom by resonance¹¹⁻¹⁴. The infrared spectroscopic investigation, however, formed part of larger programme of work involving the examination of the vibrational spectra from 4000-400cm⁻¹ of pyridine and substituted pyridines containing two, three and four substituents¹⁵⁻¹⁷. The objective of this investigation is to identify the vibrational frequencies

corresponding to each substituents whether they are stretching vibrations or associated bending vibrations. It was also studied that the vibrations are dependent on the total number of substituents and their position in the ring. Hence, the vibrational spectra of 2-hydroxy-5-methyl-3-nitro pyridine have been studied.

2 Experimental Details

The spec-pure grade sample of 2-hydroxy-5-methyl-3-nitro pyridine (hereafter referred as 2,5,3 - HMNP) has been obtained from M/s Sigma Aldrich chemical Co., USA and used as such. Its purity has been confirmed by elemental analysis and melting point determination. The FTIR spectrum of the compound 2,5,3 - HMNP has been recorded on Perkin-Elmer spectrophotometer in the region 4000-400cm⁻¹ in nujolmull. A photoconductive cell is used for detection of IR. The laser Raman spectra of the said compound was recorded in the region 4000-50cm⁻¹ on Spex-model 1403 spectrophotometer equipped with a double monochromator and computer data mate. The sample was placed in a quartz cell and to excite this 488nm line of an Ar⁺ laser was used. Both the spectra were recorded at room temperature. Resolution of spectrophotometer was of the order of 2 cm⁻¹. The time constant was kept 0.25 s and scanning speed was 100 cm⁻¹ per minute. The observed FTIR and laser Raman spectra are shown in Figures 1 and 2, respectively.

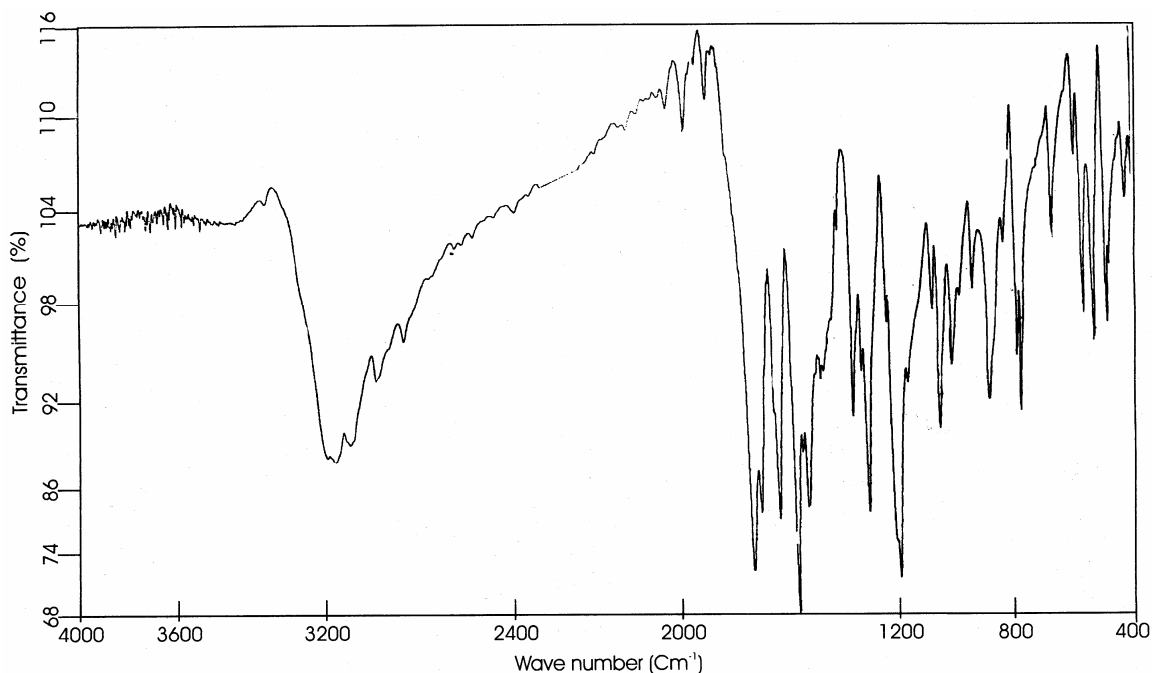


Fig. 1—FTIR Spectrum of 2, 5, 3 -HMNP

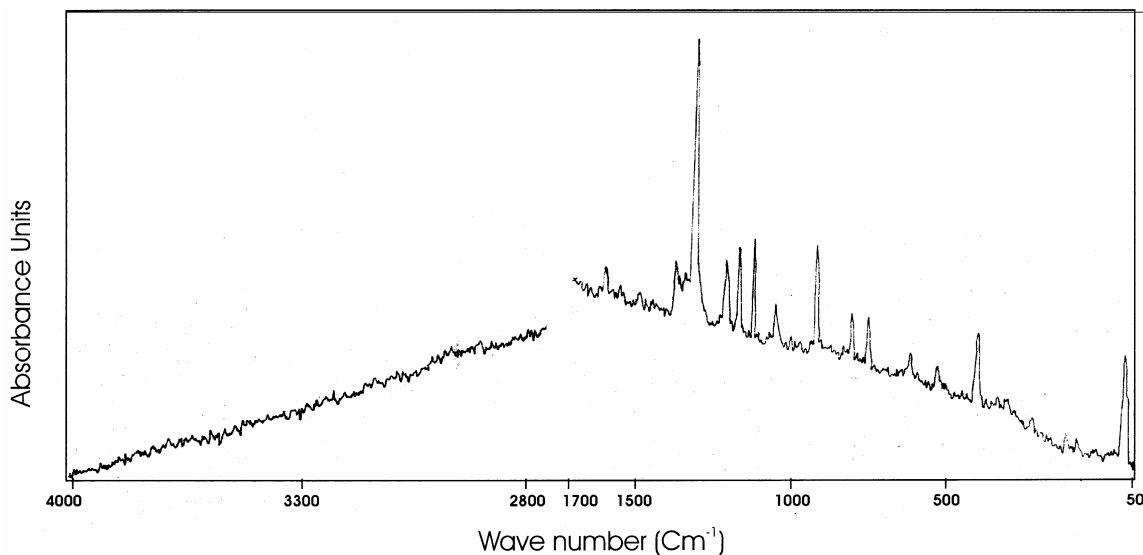


Fig. 2—Laser Raman Spectrum of 2, 5, 3 —HMNP

3 Structure and Symmetry

The molecular structure of the said molecule is shown in Figure 3. Assuming NO_2 and CH_3 as single mass point, the molecule under consideration would belong to C_s point group symmetry. The molecule has 12 atoms and one can expect 30 ($3n-6$) normal vibrations which are distributed as 22 in-plane vibrations of a^I species and 8 out-of-plane vibrations of a^{II} species as given below:

$$\Gamma = 22 a^I (\text{planer}) + 8 a^{II} (\text{non-planer})$$

All the vibrations are active in both FTIR and Raman. Apart from these vibrations, few group vibrations are also observed due to NO_2 and CH_3 groups.

4 Vibrational Assignments

The vibrational analysis of 2,5,3- HMNP are made on the basis of the magnitude and relative intensities

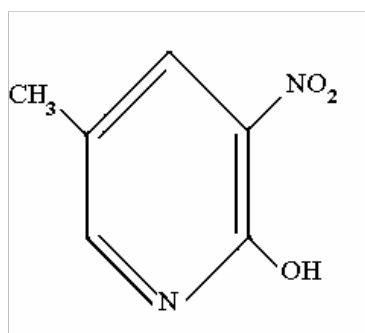


Fig.3- Molecular structure of 2,5,3 - HMNP

of the recorded spectra and in analogy with the assignments made by the earlier researchers on the similar type of molecules. The observed frequencies of 2,5,3 - HMNP together with relative intensities and probable assignments are presented in Table 1.

C-H vibrations — The two hydrogen atoms left around the ring in 2,5,3 - HMNP give rise to two C-H stretching, two C-H in-plane bending and two C-H out-of-plane bending vibrations. The heteroatomic structure shows the presence of C-H stretching vibrations in the region $3100-3000\text{cm}^{-1}$, which is the characteristic region for ready identification of C-H stretching vibrations⁹. In this region, the bands are not affected appreciably by the nature of substitutions¹². Hence, the bands at 3068cm^{-1} in IR and $3064, 3024\text{cm}^{-1}$ in Raman spectrum are assigned to C - H stretching modes in the present molecule.

Two C-H in-plane bending vibrations are also found, which are assigned at 1077cm^{-1} in FTIR spectrum and 1132cm^{-1} in laser Raman spectrum. The two C-H out-of-plane bending vibrational frequencies are assigned at 807 and 829cm^{-1} in Raman and FTIR spectra, respectively. These values are fairly agreed with the literature values¹⁶⁻¹⁹.

C-C vibrations — The ring stretching vibrations are very much prominent in the spectrum of pyridine and its derivatives and are highly characteristic of aromatic ring itself¹⁴. Benzene has two doubly degenerate vibrations e_{2g} (1596cm^{-1}) and e_{1u} (1485cm^{-1}). The doubly degenerate vibration e_{2g} (1596cm^{-1}) consists of lateral dilation and contraction of the ring produced mainly by stretching and compressing of C-C bands. Bands between $1450-1680\text{cm}^{-1}$ in benzene derivatives are assigned to these modes. The doubly degenerated e_{1u} (1485cm^{-1}) mode is basically a ring deformation since it involves both stretching and bending of carbon atoms¹¹. Hence, the bands observed at $1670, 1550$ and 1505cm^{-1} in

FTIR and 1660 and 1505cm^{-1} in Raman are assigned to C-C stretching vibrational modes.

The in-plane carbon bending vibrations are derived from non-degenerate b_{1u} (1010cm^{-1}) and degenerate e_{2g} (606cm^{-1}) modes of benzene. The non-degenerate b_{1u} (1010cm^{-1}) is observed 1016cm^{-1} and the degenerate e_{2g} (606cm^{-1}) mode has been observed at 590cm^{-1} in FTIR spectrum in this work.

The carbon out-of-plane bending vibrations are derived from the non-degenerate b_{2g} (703cm^{-1}) and degenerate e_{2u} (404cm^{-1}) modes of benzene. In this study, the carbon out-of-plane bending vibrations under Cs symmetry are observed at 747 and 499cm^{-1} in Raman and FTIR spectra, respectively. This is in good agreement with the earlier reporters²⁰⁻²⁴. Yadav *et al.*¹⁷ have assigned trigonal bending mode near 950cm^{-1} and ring breathing mode at 787cm^{-1} in 5-chloro-2,3-dihydroxy pyridine. In view of these assignments, the weak bands observed at 936 and 790cm^{-1} in FTIR represent these modes, which are given in Table 1.

C-N vibrations — The C-N stretching frequencies in the side chain are a rather difficult task¹³, since there are problems in identifying these frequencies from other vibrations. The C-N stretching usually lies in the region $1200-1400\text{cm}^{-1}$. In this work, the band observed at 1209cm^{-1} in FTIR and 1211cm^{-1} in Raman are assigned to C-N stretching vibration. The C-N in-plane bending and out-of-plane bending vibrations are assigned to 890cm^{-1} in FTIR and 342cm^{-1} in Raman, respectively. The above results are in close agreements with the literature values^{6, 12}.

Vibrations of nitro group — The nitro group substituted at the third position of the said molecule gives rise to C-NO₂ stretching vibrations in addition to the internal vibrations⁹. The FTIR very strong band appeared at 1602cm^{-1} and is assigned to C-NO₂ stretching vibrations. In the vibrational spectra of 2-chloro-3-nitro pyridine and 2-methyl-8-nitro quinoline, Medhi *et al.*⁸ and Krishnakumar *et al.*¹¹ identified the various internal vibrations of nitro group. In analogy with their study, very strong FTIR band observed at 1540cm^{-1} and a FTIR band at 1351cm^{-1} are assigned to the asymmetric and symmetric stretching, respectively of the NO₂ group. Similarly, the symmetric deformation of the NO₂ group may be identified with a very strong Raman band at 853cm^{-1} . The NO₂ wagging and rocking modes are observed at 475 and 541cm^{-1} in Raman spectra. The C-NO₂ in-plane bending and out-of-plane

Table 1 — Vibrational assignments of fundamental frequencies of 2,5,3 – HMNP

Species	Observed Frequency with Intensity		Assignments
	FTIR	Laser Raman	
a ^I	3355w	3356vw	ν(O – H)
a ^I	3068s	3064vw	ν(C – H)
a ^I	—	3024vw	ν(C – H)
—	2970s	—	ν _{asym} (CH ₃)
—	—	2911w	ν _{asym} (CH ₃)
—	2885s	—	ν _{sym} (CH ₃)
a ^I	1670vs	1660s	ν(C – C)
a ^I	1602vs	—	ν(C – NO ₂)
a ^I	1550s	1550s	ν(C – C)
—	1540vs	—	ν _{asym} (NO ₂)
a ^I	1505vs	1505w	ν(C – C)
—	1456s	1451w	β _{asym} (CH ₃)
—	1351s	1349s	ν _{sym} (NO ₂)
—	1326s	1331w	β _{sym} (CH ₃)
a ^I	1296vs	1295vs	ν(C – CH ₃)
a ^I	1209 vs	1211vs	ν(C – N)
a ^I	—	1172vs	ν(C – OH)
a ^I	1159s	1148w	β(O – H)
a ^I	—	1132vs	β(C – H)
a ^I	1077w	—	β(C – H)
—	1062s	1065s	(CH ₃)rocking
a ^I	1016s	1025w	β(C – C)
a ^I	—	953vs	(C – C – C)trigonal bending
a ^I	936w	—	(C – C – C) trigonal bending
a ^I	890s	875w	β(C – N)
—	—	853s	(NO ₂)deformation
a ^{II}	829w	—	γ(C – H)
a ^{II}	—	807s	γ(C – H)
a ^I	790w	—	ring breathing
a ^{II}	—	747w	γ(C – C)
a ^I	—	687w	β(C – NO ₂)
a ^I	669w	667w	β(C – OH)
a ^I	590vw	605w	β(C – C)
—	542w	541w	(NO ₂)wagging
a ^{II}	—	521w	γ(C – C – C)
a ^{II}	499w	494s	γ(C – C)
—	—	475w	(NO ₂)rocking
a ^I	433w	440w	β(C – CH ₃)
a ^{II}	—	342vw	γ(C – N)
a ^{II}	—	243vw	γ(O – H)
a ^{II}	—	216vw	γ(C – NO ₂)
—	—	83vs	(NO ₂) torsion

w – weak, vw – very weak, s – strong, vs – very strong, ν – stretching, β – in-plane-bending, γ – out-of-plane bending, sym.– symmetric, asym.– asymmetric

bending modes and NO₂ torsion mode also have been assigned, which are presented in Table 1. The assignments are in good agreement with those proposed in case of nitro pyridine and in nitro benzenes^{13,16}.

Vibrations of methyl group — Each methyl group has three stretching vibrations, one being symmetric and other two asymmetric. The frequencies of asymmetric vibrations are higher than the symmetric one⁸. Yadav *et al*¹⁹. have assigned asymmetric

stretching at 2965 and 2936cm⁻¹ while symmetric stretching at 2850cm⁻¹ in 4-methyl-3-nitro benzaldehyde. Verma *et al*¹⁵. have assigned these modes at 2984, 2938 and 2892 cm⁻¹ in 2-iodo-5-nitro toluene. In the present molecule, two asymmetric stretching bands one in FTIR at 2970cm⁻¹ and other in Raman at 2911 cm⁻¹ are observed. Symmetric stretching band is observed at 2885cm⁻¹ in the present case. CH₃ asymmetric and symmetric in-plane

bendings are observed at 1456 and 1326 cm^{-1} in FTIR and corresponding Raman values are 1451 and 1331 cm^{-1} , respectively. The CH_3 out-of-plane bending are also observed, which are presented in Table 1. These assignments agree well with the results of the earlier researchers²⁰⁻²¹.

In the vibration spectra of 5-methyl-2-thio uracil and 2,4 and 3,4 dimethyl phenols Yadav *et al.*⁶ and Singh *et al.*⁷ identified the C- CH_3 stretching vibration at 1215 and 1295 cm^{-1} , respectively. In view of these, a very strong band observed at 1296 cm^{-1} in FTIR with corresponding Raman value 1295 cm^{-1} , has been attributed C- CH_3 stretching mode. The C- CH_3 out-of-plane bending mode has been observed at 433 cm^{-1} in FTIR and corresponding Raman value at 440 cm^{-1} . These assignments find support with the earlier assignments made for similar molecules^{17, 24}.

Vibration of hydroxy group — In phenols, the free O-H group absorbs at 3615 cm^{-1} while the associated group has a stretching frequency in the range 3145-3430 cm^{-1} . This is due to the intermolecular hydrogen bonding¹². Yadav *et al.*¹⁷ have assigned this mode at 3227 cm^{-1} in 5-chloro-2,3-dihydroxy pyridine. Thus, the band observed at 3355 cm^{-1} in FTIR with corresponding Raman value at 3356 cm^{-1} has been taken to represent O-H stretching mode. The predominant contribution⁷ of in-plane bending vibration of OH group is always centered at around 1200 cm^{-1} . Thus, the strong band appeared in the FTIR spectrum at 1159 cm^{-1} and a very weak band at 1148 cm^{-1} in Raman spectrum has been attributed to in-plane bending vibration of OH group. The out-of-plane bending mode of hydroxyl group is assigned at 216 cm^{-1} in Raman spectra, respectively.

Some researchers²¹⁻²² have assigned C-OH stretching mode around 1200 cm^{-1} in substituted benzenes and pyridines. A very strong band observed at 1172 cm^{-1} in laser Raman spectra has been assigned to C-OH stretching mode in the present molecule. The C-OH in-plane bending mode observed at 669 cm^{-1} in FTIR and 667 cm^{-1} in Raman spectra, respectively.

Thus a complete vibrational assignments have been made available for 2-hydroxy-5-methyl-3-nitro pyridine for the first time using the frequencies obtained from the FTIR and laser Raman spectra on the basis of C_s point group symmetry.

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