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# Scaled Quantum Chemical Studies of the Structure, Vibrational Spectra of 2-Hydroxy-6-Methyl-5-Nitropyridine

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#### ABSTRACT

The vibrational spectroscopy of 2-Hydroxy-6-methyl-5-Nitropyridine (HMNP) by means of quantum chemical calculation has been studied. The FT-Raman and FT-IR spectra of HMNP have been recorded in the region 3500-50cm<sup>-1</sup> and 4000-400cm<sup>-1</sup> respectively. The fundamental vibrational frequencies and intensity of vibrational bands have been evaluated using density functional theory (DFT) with standard B3LYP/6-311+G (d,p) basis set combinations for optimized geometries. The observed FT-IR and FT-Raman vibrational frequencies have been anlaysed and compared with theoretically predicted vibrational frequencies. The assignments of bands to various normal modes of molecule have also been carried out. The electric dipole moment ( $\mu$ ) and the first hyper polarazibility ( $\beta$ ) values of the investigated molecule have been computed using DFT calculations. The calculated HOMO and LUMO energies show that charge transfer occur with in the molecule.

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# 1.Introduction

The spectroscopic study of N-heterocyclic molecules including substituted pyridines, pyrimidines have 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 interest [1-5]. The spectroscopic study of the compound has been motivated for its use to understand the specific biological process and in the analysis of relatively complex system [6-10]. In pyridine system, a large amount of intermolecular association is possible because of its greater polarity. The nitrogen atom is located in sp<sup>2</sup>-hybridized orbital, which is perpendicular to  $\pi$ -systems 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 pronotation. 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 resonance [11-13]. The infrared spectroscopic investigation, however, formed part of larger programme of work involving the examination of the vibrational spectra from 4000-400 cm<sup>-1</sup> of pyridine and substituted pyridines containing two, three and four substituents [14-16]. 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 is also studied that the vibrations are dependent on the total number of substituents and their position in the ring. Hence, a detailed quantum chemical study will aid in understanding the vibrational modes

of 2-hydroxy-6-methyl-5-nitropyridine [**HMNP**]. In the present investigation FT-IR and FT-Raman spectral analysis of HMNP molecule, have been performed using density functional theory (DFT) based on the calculated and vibrational spectral analysis.

#### 2. Experimental Details

The spec-pure grade sample of HMNP is obtained from the Lascaster Chemical Company, UK and used as such for the spectral measurements. The room temperature Fourier transform infrared spectra of HMNP is measured in the region  $4000-400 \text{ cm}^{-1}$  at a resolution of  $\pm 1 \text{ cm}^{-1}$  using a BRUKER 1FS-66V FT-IR spectrometer equipped with a cooled MCT detector for the Mid-IR region. KBr Pellet is used in the spectral measurements. Boxcar apodization is used for the 250 averaged interferograms collected for the sample and background.

The FT-Raman spectrum of HMNP is recorded on a BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory in the 3500–100 cm<sup>-1</sup> stokes region using the 1064 nm line of a Nd:YAG laser for excitation operating at 200 mw power. The reported wave numbers are believed to be accurate within  $\pm 1$  cm<sup>-1</sup>.

# 3. Computational Details

Quantum chemical density functional calculations are carried out for HMNP with the 2009 Window version of the GAUSSIAN suite program [17] using the Becke-3-Lee-Yang-Parr (B3LYP) functionals [18,19] supplemented with the standard 6-311+G(d,p) basis set (referred to as DFT calculations). All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true energy minimum, as revealed by the lack of imaginary values in the wave number calculations. The cartesian representation of the theoretical force constants have been computed at the fully optimized geometry by assuming the molecule belongs to  $C_s$  point group symmetry. The transformation of force field from cartesian to internal local-symmetry coordinates, the scaling, the subsequent normal coordinate analysis calculation of total energy distribution (TED), are done on a PC with the MOLVIB program (version V7.0-G77) written by Sundius the systematic comparison of the results of experiments has shown that the method using B3LYP functional is the most promising in providing correct vibrational wavenumbers.

# 4. Results and Discussion

#### 4.1. Molecular Geometry

The molecular structure of the said molecule is shown in Fig..1. The molecule under consideration would belong to  $C_s$  point group symmetry. The molecule has 17 atoms and one can expect 45 normal vibrations which are distributed as 31 in-plane vibrations of a' species and 14 out-of-plane vibrations of a". The global minimum energy obtained by the DFT structure optimization for HMNP is calculated as -567.2759 Hartrees. The calculated optimized geometrical parameter obtained in this study is presented in Table.1.

Table 1.Optimized geometrical parameters of 2hydroxy-6-methyl-5-nitropyridine obtained by B3LYP/6-311+G(d.p) density functional calculations.

01110	STI-G(up) density functional calculations.					
Bond length	Value (Å)	Bond angle	Value (°)			
$N_1-C_2$	1.39	$N_1-C_2-C_3$	120.00			
C <sub>2</sub> -C <sub>3</sub>	1.39	$C_2-C_3-C_4$	120.00			
C <sub>3</sub> -C <sub>4</sub>	1.39	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	119.990			
C4-C5	1.39	$C_4-C_5-C_6$	119.990			
C5-C6	1.39	C5-C6-N1	120.00			
C6-N1	1.39	$C_{6}-N_{1}-C_{2}$	120.00			
C2-O7	1.43	N <sub>1</sub> -C <sub>2</sub> -O <sub>7</sub>	119.990			
O7-H8	0.96	C <sub>3</sub> -C <sub>2</sub> -O <sub>7</sub>	120.00			
C3-H9	1.09	C2-O7-H8	109.470			
C4-H10	1.09	C2-C3-H9	119.980			
C5-N11	1.47	C4-C3-H9	120.010			
N <sub>11</sub> -O <sub>12</sub>	1.36	C <sub>3</sub> -C <sub>4</sub> -H <sub>10</sub>	120.020			
N <sub>11</sub> -O <sub>13</sub>	1.36	C5-C4-H10	119.980			
C6-C14	1.54	C4-C5-N11	119.990			
C14-H15	1.06	C6-C5-N11	120.000			
C14-H16	1.07	O <sub>12</sub> -N <sub>11</sub> -O <sub>13</sub>	120.000			
C14-H17	1.06	C5-N11-O12	119.990			
		C <sub>5</sub> -N <sub>11</sub> -O <sub>13</sub>	119.990			
		C5-C6-C14	120.010			
		$N_1-C_6-C_{14}$	119.980			
		C6-C14-H15	109.470			
		C6-C14-H16	109.470			
		C6-C14-H17	109.470			
		C14-H15-H16	95.450			
		C14-H16-H17	35.070			



Fig 1. Molecular Structure of 2-hydroxy-6-methyl-5nitropyridine.

Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose, the full set of 57 standard internal coordinates (Containing 12 redundancies) are defined in Table.2. From these, a nonredundant set of local symmetry coordinates are constructed by suitable linear combination of internal coordinates following the recommendations of Fogarasi and Pulay [20,21] are summarized in Table.3. The theoretically calculated DFT force fields are transformed to this latter set of vibrational coordinates and used in all the subsequent calculations.

Table 2.Definition of internal co-ordinates of 2hydroxy-6-methyl-5-nitropyridine.

Stretching           1         Si         O-H         O7-H8           2-3 $r_i$ C-H         C3-H9, C7-H10           4-6 $r_i$ C-H         C14-H15, C14-H16, C14-H17           (methyl)         (methyl)         (methyl)           7-9         Qi         C-N         C2-N1, C5-N11, C6-N1           10-14         Ri         C-C         C2-C3, C3-C4, C4-C5, C5-C6, C6-C14           15-16         Pi         N-O         N11-O12, N11-O13           17         Ti         C-O         C2-O7           In-plane bending         18-23 $\beta_1$ Ring         N1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5, C5-C6, N1, C6-N1-C2           24-27 $\alpha_i$ C-C-H         C2-C3-H9, C4-C3-H9, C3-C4-H10, C5-C4-H10, C5-C4-H10, C5-C4-H10, C5-C4-H10         C5-C4-H10           28-30 $\alpha_i$ C-C-H         C6-C14-H15, C6-C14-H16, C6-C14-H17, H16-C14-H17, H16-C14-H17, H16-C14-H17         H16-C14-H17           31-33 $\sigma_i$ C-C-N         C4-C5-N11, C6-C5-N11         S6 $\sigma_i$ O-N-O         O12-N11-O13         S7         Pi         N-C-C $34-35$ $\pi_i$ C-C-N         C4-C5-N11, C6-C5-N11         S6	No.(i)	S ymbol	Туре	Definition
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	St	retching		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	1	Si	O-H	O <sub>7</sub> -H <sub>8</sub>
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2-3	ri	C-H	C <sub>3</sub> -H <sub>9</sub> , C <sub>7</sub> -H <sub>10</sub>
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	4-6	ri	C-H	C <sub>14</sub> -H <sub>15</sub> , C <sub>14</sub> -H <sub>16</sub> , C <sub>14</sub> -H <sub>17</sub>
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			(methyl)	
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	7-9	Qi	C-N	$C_2$ - $N_1$ , $C_5$ - $N_{11}$ , $C_6$ - $N_1$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	10-14	Ri	C-C	C <sub>2</sub> -C <sub>3</sub> , C <sub>3</sub> -C <sub>4</sub> , C <sub>4</sub> -C <sub>5</sub> ,C <sub>5</sub> -C <sub>6</sub> , C <sub>6</sub> - C <sub>14</sub>
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	15-16	Pi	N-O	N <sub>11</sub> -O <sub>12</sub> , N <sub>11</sub> -O <sub>13</sub>
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	17	Ti	C-0	C <sub>2</sub> -O <sub>7</sub>
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	In	-plane bend	ling	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	18-23	$\beta_1$	Ring	N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> , C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> , C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> , C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub> , C <sub>5</sub> -C <sub>6</sub> , N <sub>1</sub> , C <sub>6</sub> -N <sub>1</sub> -C <sub>2</sub>
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	24-27	$\alpha_{i}$	С-С-Н	C <sub>2</sub> -C <sub>3</sub> -H <sub>9</sub> , C <sub>4</sub> -C <sub>3</sub> -H <sub>9</sub> , C <sub>3</sub> -C <sub>4</sub> -H <sub>10</sub> , C <sub>5</sub> -C <sub>4</sub> -H <sub>10</sub>
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	28-30	αi	C-C-H	C <sub>6</sub> -C <sub>14</sub> -H <sub>15</sub> , C <sub>6</sub> -C <sub>14</sub> -H <sub>16</sub> , C <sub>6</sub> -C <sub>14</sub> -
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			(methyl)	H <sub>17</sub>
$\begin{array}{ c c c c c c c c c } & H_{16}-C_{14}-H_{17} \\ \hline & H_{16}-C_{14}-H_{17} \\ \hline & 34-35 & \pi_i & C-C-N & C_4-C_5-N_{11}, C_6-C_5-N_{11} \\ \hline & 36 & \theta_i & C-C-C & C_5-C_6-C_{14} \\ \hline & 37 & \rho_i & N-C-C & N_1-C_6-C_4 \\ \hline & 38 & \sigma_i & O-N-O & O_{12}-N_{11}-O_{13} \\ \hline & 39-40 & \phi_i & C-N-O & C_5-N_{11}-O_{12}, C_5-N_{11}-O_{13} \\ \hline & 41 & \phi_i & N-C-O & N_1-C_2-O_7 \\ \hline & 42 & \gamma_i & C-C-O & C_3-C_2-O_7 \\ \hline & Out-of-plane bending \\ \hline & 43 & \psi_i & C-O-H & C_2-O_7-H_8 \\ \hline & 44-45 & \omega_i & C-H & H_9-C_3-C_2-C_4, H_{10}-C_4-C_3-C_5 \\ \hline & 46 & \omega_i & C-N & N_{11}-C_5-C_4-C_6 \\ \hline & 47 & \omega_i & C-C & C_{14}-C_6-C_5-N_1 \\ \hline & 48 & \omega_i & O-C & O_7-C_2-C_3-N_1 \\ \hline & 49 & \omega_i & O-H & H_8-O_7-C_2-N_1(C_3) \\ \hline & Torsion \\ \hline & Torsion \\ \hline & S0-55 & t_I & Ring & N_1-C_2-C_3-C_4, C_2-C_3-C_4-C_5, \\ \hline & C_5-C_6-N_1-C_2, C_6-N_1-C_2-C_3 \\ \hline & 56 & t_i & CC-NO_2 & C_5-N_{11}-O_{12}-O_{13} \\ \hline & 57 & t_1 & CC-CH_3 & C_5(N_1) - C_6-C_{14}-(H_{15}-H_{16}-H_{17}) \\ \hline \end{array}$	31-33	σi	Н-С-Н	$H_{15}$ - $C_{14}$ - $H_{16}$ , $H_{15}$ - $C_{14}$ - $H_{17}$ ,
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				$H_{16}$ - $C_{14}$ - $H_{17}$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	34-35	$\pi_{i}$	C-C-N	C4-C5-N11, C6-C5-N11
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	36	$\theta_i$	C-C-C	C5-C6-C14
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	37	ρί	N-C-C	N <sub>1</sub> -C <sub>6</sub> -C <sub>4</sub>
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	38	σi	O-N-O	O <sub>12</sub> -N <sub>11</sub> -O <sub>13</sub>
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	39-40	φi	C-N-O	C <sub>5</sub> -N <sub>11</sub> -O <sub>12</sub> , C <sub>5</sub> -N <sub>11</sub> -O <sub>13</sub>
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	41	φi	N-C-O	N <sub>1</sub> -C <sub>2</sub> -O <sub>7</sub>
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	42	γ <sub>i</sub>	C-C-O	C <sub>3</sub> -C <sub>2</sub> -O <sub>7</sub>
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O	ut-of-plane	bending	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	43	Ψi	С-О-Н	C2-O7-H8
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	44-45	ωi	C-H	H9-C3-C2-C4, H10-C4-C3-C5
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	46	ωi	C-N	N <sub>11</sub> -C <sub>5</sub> -C <sub>4</sub> -C <sub>6</sub>
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	47	ω <sub>i</sub>	C-C	C <sub>14</sub> -C <sub>6</sub> -C <sub>5</sub> -N <sub>1</sub>
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	48	ω <sub>i</sub>	O-C	O <sub>7</sub> -C <sub>2</sub> -C <sub>3</sub> -N <sub>1</sub>
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	49	ω <sub>i</sub>	O-H	$H_8-O_7-C_2-N_1(C_3)$
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Тс	orsion		
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	50-55	tI	Ring	N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> , C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> ,
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$			C C	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub> , C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub> -N <sub>1</sub> ,
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				C <sub>5</sub> -C <sub>6</sub> -N <sub>1</sub> -C <sub>2</sub> , C <sub>6</sub> -N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>
57 $t_{I}$ CC-CH <sub>3</sub> C <sub>5</sub> (N <sub>1</sub> ) -C <sub>6</sub> -C <sub>14</sub> -(H <sub>15</sub> -H <sub>16</sub> -H <sub>17</sub> )	56	ti	CC-NO <sub>2</sub>	C5-N11-O12-O13
	57	tI	CC-CH <sub>3</sub>	$C_5(N_1) - C_6 - C_{14} - (H_{15} - H_{16} - H_{17})$

For numbering of atom refer fig. 1.



Fig 2. FT-IR spectrum of 2-hydroxy-6-methyl-5nitropyridine.

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Table 3. Definition of local symmetry	y co-ordinates	and values	of corresponding	scale factors	used to	correct the	refined and
B3LYP/6-3	511+G(d,p) for	ce fields for	· 2-hydroxy-6-met	hyl-5-nitropy	ridine.		

No.(i)	S ymbol <sup>a</sup>	Definition <sup>b</sup>	Scale factors used in the Calculation
			B3LYP / 6-311+G(d,p)
1	OH	<b>S</b> <sub>1</sub>	0.983
2-3	СН	r <sub>2</sub> , r <sub>3</sub>	0.983
4	CH <sub>3</sub> SS	$(r_4 + r_5 + r_6) / \sqrt{3}$	0.976
5	CH <sub>3</sub> ips	$(2r_4 + r_5 + r_6) / \sqrt{6}$	0.976
6	CH <sub>3</sub> ops	$(r_5 - r_6) / \sqrt{2}$	0.976
7-9	CN	$Q_7, Q_8, Q_9$	0.983
10-14	CC	$R_{10}, R_{11}, R_{12}, R_{13}, R_{14}$	0.983
15	NO <sub>2</sub> ss	$(P_{15} + P_{16})/\sqrt{2}$	0.920
16	NO <sub>2</sub> ips	$(P_{15} - P_{16})/\sqrt{2}$	0.920
17	CO	T <sub>17</sub>	0.983
18	R trigd	$(\beta_{18}\!-\!\beta_{19}\!+\!\beta_{20}\!-\!\beta_{21}\!+\!\beta_{22}\!-\!\beta_{23})\!/\sqrt{6}$	0.967
19	R symd	$(-\beta_{18}\!-\!\beta_{19}\!+\!2\beta_{20}\!-\!\beta_{21}\!-\!\beta_{22}\!+\!2\beta_{23})/\sqrt{12}$	0.967
20	R asymd	$(\beta_{18} - \beta_{19} + \beta_{21} - \beta_{22})/2$	0.967
21-22	b CH	$\left( \alpha_{24}\!-\!\alpha_{25}  ight)/\sqrt{2}$ , $\left( \alpha_{26}\!-\!\alpha_{27}  ight)\!/\sqrt{2}$	0.982
23	CH <sub>3</sub> sb	$(-\alpha_{28}-\alpha_{29}-\alpha_{30}+\delta_{31}+\delta_{32}+\delta_{33})/\sqrt{6}$	0.978
24	CH <sub>3</sub> ipb	$(-\delta_{31} - \delta_{32} - 2\delta_{33})/\sqrt{6}$	0.978
25	CH <sub>3</sub> ipb	$(\delta_{31} - \delta_{32})/\sqrt{2}$	0.978
26	CH <sub>3</sub> ipr	$(2\alpha_{28} - \alpha_{29} - \alpha_{30})/\sqrt{6}$	0.978
27	CH <sub>3</sub> opr	$(\alpha_{29} - \alpha_{30})/\sqrt{2}$	0.978
28	b CN	$(\pi_{34} - \pi_{35})/\sqrt{2}$	0.982
29	b CC	$(\theta_{36}-\theta_{37})/\sqrt{2}$	0.982
30	NO <sub>2</sub> sciss	$(2\sigma_{\!38}-\phi_{\!39}-\phi_{\!40})\!/\sqrt{6}$	0.876
31	NO <sub>2</sub> Rock	$(\phi_{39} - \phi_{40})/\sqrt{2}$	0.876
32	NO <sub>2</sub> twist	$(\phi_{39} + \phi_{40}) / \sqrt{2}$	0.876
33	bCO	$(\phi_{41}-\gamma_{42})/\sqrt{2}$	0.982
34	bOH	$\psi_{43}$	0.982
35-36	ωCH	$\omega_{44}, \omega_{45}$	0.935
37	ωCN	$\omega_{46}$	0.935
38	ωCC	ω <sub>47</sub>	0.935
39	ωΟϹ	ω <sub>48</sub>	0.935
40	ωOH	(W <sub>49</sub>	0.935
41	tR trig	$(\tau_{50} - \tau_{51} + \tau_{52} - \tau_{53} + \tau_{54} - \tau_{55})/\sqrt{6}$	0.923
42	tR sym	$(\tau_{50} - \tau_{51} + \tau_{53} - \tau_{54})/\sqrt{2}$	0.953
43	tR asym	$(-\tau_{50}+2\tau_{51}-\tau_{52}-\tau_{53}+2\tau_{54}-\tau_{55})/\sqrt{12}$	0.923
44	NO <sub>2</sub> Wag	τ <sub>56</sub>	0.831
45	t CH <sub>3</sub>	τ <sub>57</sub>	0.923

<sup>a</sup>These symbols are used for description of normal nodes by TED in Table .4. <sup>b</sup>The internal coordinates used here are defined in Table .2.

#### 5. Vibrational Spectra

The vibrational analysis of HMNP are made the basis of the magnitude and relative intensity of the recorded spectra and in analogy with the assignment made by the earlier researchers on the similar type of molecules. The FT-IR and FT-Raman spectra of HMNP are shown in Figs..2 and.3, respectively. The detailed vibrational assignments of fundamental modes of HMNP along with the observed and calculated frequencies and normal mode descriptions (characterized by TED) are reported in Table .4.

#### **C-H Vibrations**

The two hydrogen atoms left around the ring in HMNP give rise to two C–H stretching, two C–H in-plane bending and two C–H out-of-plane bending vibrations. The hetroatomic structure shows the presence of C–H stretching vibrations in the region 3100-3000 cm<sup>-1</sup>, which is the characteristic region for ready identification of C–H stretching



Fig. 3: FT-Raman Spectrum of 2-hydroxy-6-methyl-5nitropyridine

Vibrations [10], in this region, the bands are not affected appreciably by the nature of substitutions [12]. Hence, the bands at 3002 cm<sup>-1</sup> in IR and 3084 cm<sup>-1</sup> in Raman spectrum are assigned to C–H stretching vibrations of HMNP. The C–H in-plane bending vibrations are observed at 1243 cm<sup>-1</sup> and 1210 cm<sup>-1</sup> in FT-IR and FT-Raman spectrum respectively for HMNP. The C–H out-of-plan bending vibrations are observed at 958, 932 cm<sup>-1</sup> in FT-IR spectrum of HMNP.

#### CH<sub>3</sub> Vibrations

For the assignments of  $CH_3$  group frequencies, nine fundamental vibrations can be associated to each  $CH_3$  group. Three stretching, three bending, two rocking modes and single torsional mode describe the motion of the methyl group. The  $CH_3$  symmetric stretch, frequency is established at 2912 cm<sup>-1</sup> in IR and  $CH_3$  in-plane stretch, frequencies are assigned at 2939 cm<sup>-1</sup> in IR for the title compound [22]. These assignments are also supported by the literatures [23,24] in addition to TED output.

 Table 4. Assignment of fundamental vibrations of 2-hydroxy-6-methyl-5-nitropyridine by normal mode analysis based on SQM force field calculations using selectively scaled B3LYP/6-311+G(d,p) force field.

Symmetry Species	Observed fundamen (cm <sup>-1</sup> )	tals	Calculated frequencies using B3LYP/6-311+G(d,p) force field (cm <sup>-1</sup> )		Assignments with TED(%) among types of internal coordinates
0,	FT-IR	FT- Raman	Unscaled	Scaled	
Δ'	3415(w)	-	3560	3420	vOH (99)
A'	-	3084(w)	3247	3088	vCH (97)
A'	3002(vw)	-	3151	3002	vCH (94)
A'	2939 (w)	-	3082	2936	CH <sub>3</sub> ips (90)
A'	2912(ms)	-	3073	2910	CH <sub>3</sub> ss (88)
A'	-	1623(s)	1763	1627	vCC (87)
A'	1599 (w)	-	1676	1594	vCC (89)
A'	-	1587(ms)	1647	1587	vCC (85)
A'	-	1545(s)	1608	1549	vCC (82)
A'	-	1525(ms)	1597	1520	vCC (83)
A'	1503 (S)	-	1566	1500	NO <sub>2</sub> ass (84)
A'	1430(m)	-	1491	1432	CH <sub>3</sub> ipb (81)
A'	-	1426(ms)	1474	1425	vCN (80)
A'	-	1399(s)	1438	1405	vCN (78)
A'	1378(m)		1418	1375	NO <sub>2</sub> ss (79)
A'	-	1361(m)	1388	1365	$CH_3sb(76)$
A'	1347(s)	-	1388	1350	vCO (74)
A'	-	1344(vs)	1377	1344	vCN (73)
A'	1243(vs)	-	1272	1252	bCH (72)
A'	-	1210(ms)	1235	1205	bCH (71)
A'	-	1190(s)	1226	1187	bOH (70)
A'	1127(vw)	-	1162	1126	R trigd(71)
A'	1096(vs)	-	1121	1097	R symd(72)
A'	-	1038(m)	1065	1042	R asymd(73)
A'	1032(s)		1050	1024	CH <sub>3</sub> ipr (70)
A'		928(w)	947	924	bCN (69)
A'		799(w)	819	802	bCO (68)
A'	767(s)		788	767	$NO_2$ sciss (69)
A'	602(vw)	-	620	595	bCC (67)
A'		548(s)	561	552	NO <sub>2</sub> rock (69)
A″	2729(vw)		2758	2728	CH <sub>3</sub> ops (65)
Α"	1194(m)		1216	1194	CH <sub>3</sub> opb(63)
A″	-	998(ms)	1015	995	CH <sub>3</sub> opr (64)
A″	958(m)	-	978	954	ωCH (62)
A″	932(m)		944	930	ωCH (64)
A″	726(ms)	-	744	731	NO <sub>2</sub> wag (61)
A″		663(s)	676	661	tRtrigd(60)
A″	639(vs)		649	642	tR symd(62)
A″	543(m)		552	542	tRasymd(61)
A″	470(w)		474	471	ωCN (58)
Α"		460(s)	473	460	ωCC (59)
A″		414(m)	414	416	ωCO (57)
A″		358(s)	366	356	ωOH (59)
A‴		331(w)	334	335	NO <sub>2</sub> twist (56)
Α"		253(vw)	249	252	tCH <sub>3</sub> (54)

Abbreviations:R - ring; b - bending; ω - out-of-plane bending; t - torsion; trigd - trigonal deformation; symd - symmetric deformation; ss - symmetric stretching; ass - asymmetric stretching; asymd - anti symmetric deformation; ibs - in-plane stretching;

vs - very strong; s - strong; m - medium; w - weak; vw - very weak.



Fig 4. The atomic orbital compositions of the frontier molecular orbital of 2-hydroxy-6-methyl-5-nitropyridine.

The two in-plane methyl hydrogen deformation modes are also well established. The symmetrical methyl bending mode at 1361 cm<sup>-1</sup> in the Raman and out-of-plane bending mode observed at 1194 cm<sup>-1</sup> in IR, the band at 2729 cm<sup>-1</sup> in infrared is attributed to CH<sub>3</sub> out-of-plane stretching mode in the A" species. The methyl deformation modes mainly coupled with in-plane bending vibrations. The band obtained at 1032 cm<sup>-1</sup> in IR and 998 cm<sup>-1</sup> in Raman are assigned to CH<sub>3</sub> in-plane and out-of-plane rocking modes. The assignment of the band at 253 cm<sup>-1</sup> in Raman is attributed to methyl twisting mode. The CH<sub>3</sub> in-plane bending mode obtained at 1430 cm<sup>-1</sup>.

#### **C–N Vibrations**

The C–N stretching frequencies in the side chain are a rather difficult task [25]. Since there are problems in identifying these frequencies from other vibrations, the C–N stretching usually lies in the region  $1400-1200 \text{ cm}^{-1}$ . In this study, the band observed at  $1426 \text{ cm}^{-1}$ ,  $1399 \text{ cm}^{-1}$  and  $1344 \text{ cm}^{-1}$  in Raman are assigned to C–N stretching vibrations. The C–N bending vibration and deformation modes are assigned to 928 cm<sup>-1</sup> in Raman and 470 cm<sup>-1</sup> in IR The above results are in close agreement with literature values [7,12].

#### NO<sub>2</sub> Vibrations

The nitro group substituted at the fifth position of the title compound gives rise to C–NO<sub>2</sub> stretching vibrations. In the vibrational spectra of 2-Chloro-3-nitropyridine and 2-methyl-8-nitroquinoline, Sharma *et al.*, [9] and Arivazhagan *et al.*, [26] identified the various internal vibrations of nitro group. In analogy with their study, the FT-IR band observed at 1503 cm<sup>-1</sup> and 1378 cm<sup>-1</sup> are assigned to the asymmetric and symmetric stretching, respectively of the NO<sub>2</sub> scissoring group may be identified with a strong FT-IR band observed at 767 cm<sup>-1</sup>. The NO<sub>2</sub> wagging and rocking modes are observed at 726 cm<sup>-1</sup> in FT-IR and 548 cm<sup>-1</sup> in Raman spectra. The NO<sub>2</sub> twisting mode is observed at 331 cm<sup>-1</sup> in Raman. The assignments are in good agreements with those proposed in case of nitropyridine and in nitro benzenes [14,25].

#### **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 itself [14]. The bands between 1400 and 1650 cm<sup>-1</sup> in benzene derivatives are due to C–C stretching vibrations [27]. In this study the bands between 1599 cm<sup>-1</sup> and 1623–1525 cm<sup>-1</sup> in FT-IR and FT-Raman spectra of title compound respectively. The higher percentage of total energy distribution (TED) obtained for this group encouraging and confirms the assignments proposed in this study for C-C stretching vibrations.

#### 6. HOMO-LUMO Analysis

The interaction of two atomic (or) molecular orbitals produces two new orbital. One of the new orbitals is higher in energy than the original ones (the anti bonding orbital) and one is lower (the bonding orbital). When one of the initial orbitals is filled with a pair of electrons (a Lewis base) and the other is empty (a Lewis acid), we can place the two electrons into the lower, energy of the two new orbitals. The "filledempty" interaction therefore is stabilizing. When we are dealing with interacting molecular orbitals, the two that interact are generally the highest energy occupied molecular orbital (LUMO) of the molecule. These orbitals are the pair of orbitals in the molecule, which allows them to interact most strongly. These orbitals are sometimes called the frontier orbitals, because they lie at the outermost boundaries of the electrons of molecule. The HOMO-LUMO analysis for the title molecule has been carried out using B3LYP/6-311++G(d,p) level.

By contrast, the HOMO is located over methyl and NO<sub>2</sub> atoms; whereas LUMO is located on ring and methyl group atoms of 2-hydroxy-6-methyl-5-nitropyridine. The atomic orbital compositions of the frontier molecular orbital are shown in Fig. 5.4. The HOMO  $\rightarrow$  LUMO energy gap of 2-hydroxy-6-methyl-5-nitropyridine obtained by B3LYP/6-311+G(d,p) density functional calculations, reveals that the energy gap reflects the chemical activity of the molecules. The LUMO as an electron acceptor (EA) represents the ability to obtain an electron (ED), and HOMO represents the ability to donate an electron(ED). The ED groups to the efficient EA groups through  $\pi$ -conjugated path.

0 1 0	50 1
Еномо	= -0.300458 a.u.
Elumo	= -0.148682 a.u.
Energy gap	= 0.151776 a.u.

The energy gap explains the fact that eventual charge transfer interaction is taking place within the molecule.

#### 7. Vibrational Contribution To Nlo Activity And First Hyperpolarizability

Non-linear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields [28]. Organic molecules with significant non-linear optical activity generally consist of a p electron conjugated moiety substituted by an electron donor group on one end of the conjugated structure and an electron acceptor group on the other end, forming a 'push-pull' conjugated structure [29]. The total static dipole moment ( $\mu$ ) and the first hyperpolarizability ( $\beta$ ) using the x, y, z components are defined as [30].

... (1)

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

The dipole moment ( $\mu$ ) and the first hyperpolarizability ( $\beta$ ) have been calculated at the B3LYP/6-311++G(d,p) level using GAUSSIAN 09W program package. The calculated total dipole moment ( $\mu$ ) and mean first hyperpolarizability ( $\beta$ ) of HMNP are 4.1593 Debye and 5.7404 × 10<sup>-30</sup> esu, respectively, which is comparable with the **r**eported values of similar derivatives. The large value of hyperpolarizability,  $\beta$  which is

a measure of the non-linear optical activity of these molecular systems, are associated with the intramolecular charge transfer, resulting from the electron cloud movement through  $\pi$  conjucated frame work from electron donar to electron acceptor groups. So the title compound is an attractive object for future studies of nonlinear optical properties.

#### 8. Other Molecular Properties

The thermodynamic properties like heat capacity, zero point energy, entropy along with the global minimum energy of HMNP have been obtained by density functional method using 6-311+G(d,p) basis set calculations are presented in Table 5. The difference in the values calculated by both the methods is only marginal. Scale factors have been recommended for an accurate prediction in determining the zero-point vibration energy (ZPVE), and the entropy ( $S_{vib}$ ). The variation in the ZPVE seems to be insignificant.

The total energy and the change in the total entropy of the compounds at room temperature are also presented.

Table	5.The	thermodynamic	parameters	of 2-hydroxy-
		6-methyl-5-nitro	pyridine.	

	Method/Basis
Devenuetors	set
rarameters	B3LYP/6-
	311+G(d,p)
Total energy (thermal), E <sub>total</sub> (kcal mol <sup>-1</sup> )	81.659
Heat capacity, $C_v$ (kcal mol <sup>-1</sup> k <sup>-1</sup> )	30.454
Entropy, S (kcal mol <sup><math>-1</math></sup> k <sup><math>-1</math></sup> )	
Total	88.169
Translational	41.006
Rotational	30.050
Vibrational	17.112
Vibrational energy, E <sub>vib</sub> (kcal mol <sup>-1</sup> )	79.882
Zero point vibrational energy, (kcal mol <sup>-1</sup> )	76.77757
Rotational constants (GHz)	
A	2.38839
В	0.78383
С	0.59256
Dipolemoment (Debye)	
μ <sub>x</sub>	-3.1776
μ <sub>v</sub>	-2.5649
μ <sub>z</sub>	-0.7894
µ <sub>total</sub>	4.1593

Conclusion

The SQM force field method based on DFT calculations at the B3LYP/6-311+G(d,p) level have been carried out to analyze the vibrational frequencies of 2-hydroxy-6-methyl-5-nitropyridine. The close agreement established between the experimental and scaled frequencies obtained using the large basis set (6-311+G(d,p)) calculation is proved to be more reliable and accurate than the calculation of semi empirical methods (or) lower basis sets. This accuracy is desirable for resolving distributes in vibrational assignments and provides valuable insight for understanding the observed spectral features. The energy gap explains the fact that eventual charge transfer interaction is taking place within the molecule. The thermodynamic properties and NLO properties of the molecule have also been studied.

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