

## Experimental Study (FT IR and FT Raman), Computed Vibrational Frequency Analysis and Computed IR Intensity and Raman Activity Analysis on 2, 6-Lutidine: HF and DFT Calculations

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### Abstract

In this work, the experimental and theoretical study on molecular structure and vibrations of 2,6-Lutidine(2,6-Ltn) are presented. The FTIR and FTRaman experimental spectra of the 2,6-Ltn have been recorded in the range of 4000-100 cm<sup>-1</sup>. Making use of the recorded data, the complete vibrational assignments are made and analysis of the observed fundamental bands of molecule is carried out. The experimental determinations of vibrational frequencies are compared with those obtained theoretically from ab initio HF and DFT quantum mechanical calculations at HF/6-31+G (d, p), B3LYP/6-31++G (d, p) and B3LYP/6-311++G (d, p) levels. The differences between the observed and scaled wave number values of most of the fundamentals are very small in DFT. The geometries and normal modes of vibrations obtained from ab initio HF and B3LYP calculations are in good agreement with the experimentally observed data. Comparison of the simulated spectra provides important information about the ability of the computational method (B3LYP) to describe the vibrational modes. The vibrations of couple of CH<sub>3</sub> groups with skeletal vibrations are also investigated.

**Key words:** ab-initio HF, Couple of CH<sub>3</sub> groups, FT IR, FT Raman, 2,6-Lutidine, vibrational modes and DFT.

### 1. Introduction

The pyridine derivatives have an important position among the heterocyclic compounds because they can be used as nonlinear materials and photo chemicals. In particular, some of these crystals have been reported as frequency converters from NIR to the visible wavelength region [1-2]. Pyridine heterocycles and its derivatives are a repeated moiety in many large molecules with interesting photo chemical, electrochemical and catalytic applications [3-8]. They serve as good anesthetic agent and hence are used in the preparation of drugs for certain brain

disease. These pharmaceutically acceptable pre drugs are used for the treatment (or) prevention of diabetic neuropathy [9-10]. The methyl substituent on the molecule shows some differences in the photo physical properties relative to the pyridine. 2,6Ltn constitutes an important class of heterocyclic organic compounds. Investigations on the structure of these organic molecules have been a subject of great interest because of their peculiar photo physical properties and pharmaceutical importance [11-12].

The vibrational spectra of 3-methyl pyridine have been investigated by several authors [13-15]. The FT-IR and FT-Raman spectra of 2, 3-Lutidine (Dimethyl pyridine) have been reported [16-17] together with the vibrational assignments of the vibrational modes. More recently, the molecular vibrations of 2-methyl pyridine were investigated by means of a scaled DFT analysis. The initial harmonic force field was also evaluated at B3LYP/B3PW91 (DFT) level using 6-31+G (d, p) and 6-311++G (d, p) basis sets [18]. However, the detailed HF/B3LYP comparative studies on the complete FTIR and FTRaman spectra of 2, 6-Lutidine at 6-31+G (d, p), 6-31++G (d, p) and 6-311++G (d, p) basis sets have not been reported so far.

In this study, molecular geometry, optimized parameters and vibrational frequencies are computed and the performance of the computational methods for HF and B3LYP at 6/31++G (d, p) and 6/311++G (d, p) basis sets are compared. These methods predict relatively accurate molecular structure and vibrational spectra with moderate computational effort. In particular, for polyatomic molecules the DFT methods lead to the prediction of more accurate molecular structure and vibrational frequencies than the conventional ab initio Hartree-Fock calculations. Among DFT calculation, Becke's three parameter hybrids functional combined with the Lee-Yang-Parr correlation functional (B3LYP) is the best predicting results for molecular geometry and vibrational wave numbers for moderately larger molecule [19-20].

## 2. Experimental Details

The compound under investigation namely 2,6Ltn is purchased from Sigma Aldrich chemicals, U.S.A. which is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The FTIR spectrum of the compound is recorded in Bruker IFS 66V

spectrometer in the range of 4000-100  $\text{cm}^{-1}$ . The spectral resolution is  $\pm 2\text{cm}^{-1}$ . The FT- Raman spectrum of this compound is also recorded in the same instrument with FRA 106 Raman module equipped with Nd: YAG laser source operating at 1.064  $\mu\text{m}$  line widths with 200mW power. The spectra are recorded in the range of 4000 - 100  $\text{cm}^{-1}$  with scanning speed of 30 $\text{cm}^{-1}\text{min}^{-1}$  of spectral width 2  $\text{cm}^{-1}$ . The frequencies of all sharp bands are accurate to  $\pm 1\text{cm}^{-1}$ .

## 3. Computational methods

The molecular structure of the 2,6Ltn in the ground state is computed by performing both ab initio-HF and DFT/B3LYP with 6-31+ G (d, p), 6-31++ G (d, p) and 6-311++G (d, p) basis sets. The optimized structural parameters are used in the vibrational frequency calculations at HF and DFT levels. The minimum energy of geometrical structure is obtained by using level B3LYP/6-31++ G (d, p) and B3LYP/6-311++G (d, p) basis sets. Therefore, we had a discussion on calculated values using these sets. The calculated frequencies are scaled by 0.899, 0.898 and 0.897 for HF [21-22]. For B3LYP with 6-31++G (d, p) set is scaled with 0.947, 0.957, 0.979, 0.966 and 0.927 and 6-311++G (d, p) basis set is scaled with 0.957, 0.988, 0.978, 0.960 and 0.989 [23-24]. HF calculations for 2,6Ltn are performed using GAUSSIAN 03 W program package on Pentium IV processor personal computer without any constraint on the geometry [25, 26].

## 4. Results and Discussion

### 4. 1. Molecular Geometry

The molecular structure of the 2,6Ltn belongs to  $C_{2v}$  point group symmetry. The optimized molecular structure of title molecule is obtained from GAUSSAN 03 and GAUSSVIEW programs are shown in the Fig. 1. The molecule contains couple of methyl groups connected with pyridine ring. The structure optimization zero point vibrational energy of the title compound in HF/6-31+G (d, p), B3LYP/6-31++G (d, p) and B3LYP/6-311++G (d, p) are - 402894.0, - 376060.3 and - 374622.6 joules/Mol and 96.29,

89.88 and 89.53 Kcal/mol respectively. The comparative optimized structural parameters such as bond lengths, bond angles and dihedral angles are presented in table 1. From the theoretical values, it is found that most of the optimized bond lengths are slightly larger than the experimental values, due to that the theoretical calculations belong to isolated molecules in gaseous phase and the experimental results belong to molecules in solid state[27]. Comparing bond angles and lengths of B3LYP with those of HF, as a whole the formers are bigger than later and the B3LYP calculated values correlates well compared with the experimental data. Although the differences, calculated geometrical parameters represent a good approximation and they are the bases for the calculating other parameters, such as vibrational frequencies and thermodynamics properties. The comparative bond length, bond angle and dihedral angle graphs are given in the Figs. 2, 3 and 4.

The pyridine ring appears little distorted and angles slightly out of perfect heterocyclic structure. It is obviously due to the substitution of CH<sub>3</sub> groups in the place of H atoms. The order of the optimized bond lengths of the C-C and C-N bonds of the ring as N1-C2= N1-C6<C3-C4=C4-C5<C2-C3= C5-C6. The bond lengths of N1-C2 and N1-C6 are reduced in size because of symmetrical substitution of CH<sub>3</sub> groups in heterocyclic ring. In this case, the bond lengths of N1-C6 and N1-C2 are 0.004Å shorter than the recorded X-ray data [28-29]. The optimized C-N bond length of 1.324 Å by HF methods for 2,6Ltn, underestimated by 0.023 Å with that of crystal data of pyridine at 1.347 Å [30] whereas the C-N bond lengths are underestimated by 0.004 and 0.008 Å respectively by DFT/6-31++G (d, p) and DFT/6-311++G methods. The experimental value of C-H bond is 1.093 Å [31] of methyl group perfectly coincides with two C-H bond

values and remaining one (1.070 Å) differed by 0.023 Å (calculated by B3LYP/6-311++G (d, p)).

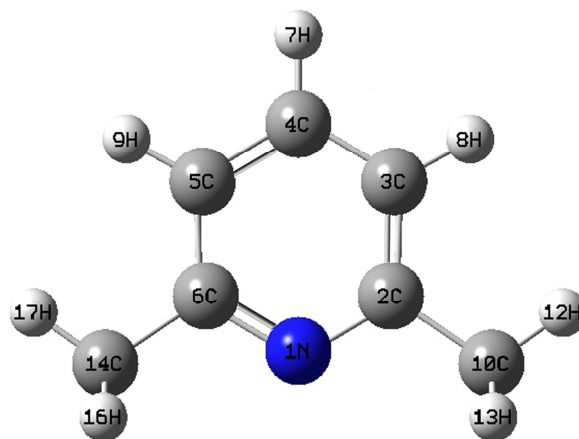


Fig. 1. Molecular structure of 2,6-Lutidine

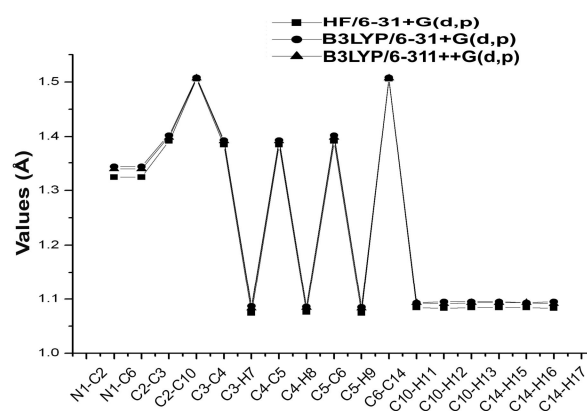


Fig. 2. Bond length differences from theoretical (HF/DFT) approaches

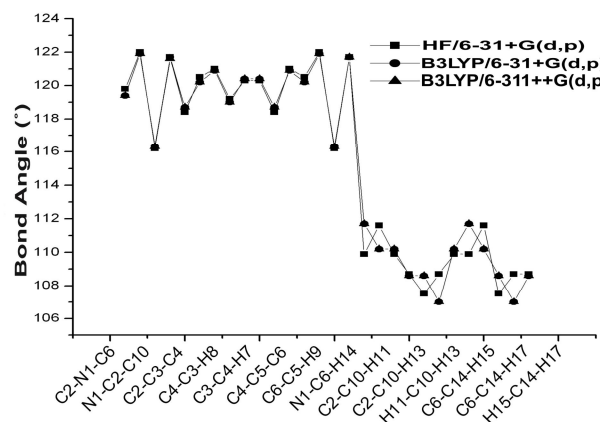
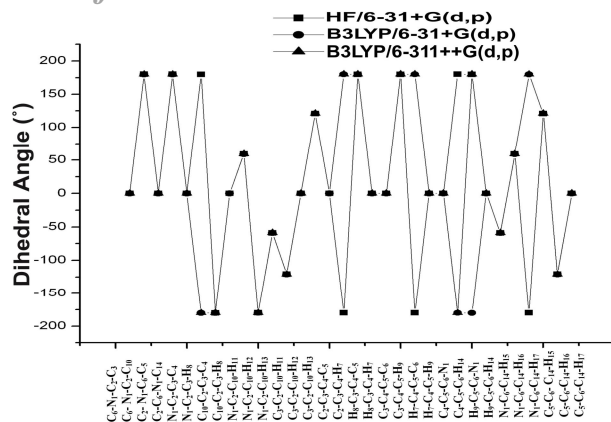


Fig. 3. Bond angle differences from theoretical (HF/DFT) approaches

**Table 1.** Optimized geometrical parameters for 2, 6-Lutidine computed at HF/6-31+G (d, p), B3LYP/6-31++G (d, p) and 6-311++G (d, p) basis set

Bond length(Å) Exp*( )	Value		Bond angle(°) Exp*( )	Value		Dihedral angles(°)	Value	
	HF/6- 31+G (d, p)	B3LYP/6- 31++G /311++G (d, p)		HF/6- 31+G (d, p)	B3LYP/6- 31++G /311++G (d, p)		HF/6- 31+G (d, p)	B3LYP/6- 31++G /311++G (d, p)
N <sub>1</sub> -C <sub>2</sub> (1.347)	1.324	1.343/1.339	C <sub>2</sub> -N <sub>1</sub> - C <sub>6</sub> (120.7)	119.8	119.4/119.4	C <sub>6</sub> -N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	0.01	0.001/0.0
N <sub>1</sub> -C <sub>6</sub> (1.347)	1.324	1.343/1.339	N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	122.0	121.9/121.9	C <sub>6</sub> -N <sub>1</sub> -C <sub>2</sub> -C <sub>10</sub>	180.0	179.92/179.9
C <sub>2</sub> -C <sub>3</sub> (1.375)	1.390	1.402/1.398	N <sub>1</sub> -C <sub>2</sub> -C <sub>10</sub>	116.2	116.3/116.3	C <sub>2</sub> -N <sub>1</sub> -C <sub>6</sub> -C <sub>5</sub>	0.01	0.001/0.0
C <sub>2</sub> -C <sub>10</sub> (1.506)	1.506	1.508/1.507	C <sub>3</sub> -C <sub>2</sub> -C <sub>10</sub>	121.7	121.7/121.6	C <sub>2</sub> -C <sub>6</sub> -N <sub>1</sub> -C <sub>14</sub>	180.0	179.9/179.9
C <sub>3</sub> -C <sub>4</sub> (1.393)	1.383	1.393/1.390	C <sub>2</sub> -C <sub>3</sub> - C <sub>4</sub> (119.2)	118.4	118.7/118.7	N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	-0.02	-0.0/-0.0
C <sub>3</sub> -H <sub>8</sub> (0.98)	1.074	1.087/1.083	C <sub>2</sub> -C <sub>3</sub> -H <sub>8</sub>	120.5	120.2/120.2	N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>8</sub>	179.9	-180.0/-180.0
C <sub>4</sub> -C <sub>5</sub> (1.393)	1.383	1.393/1.390	C <sub>4</sub> -C <sub>3</sub> -H <sub>8</sub>	121.0	120.9/120.9	C <sub>10</sub> -C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	- 180.0	-179.95/- 179.91
C <sub>4</sub> -H <sub>7</sub> (0.980)	1.076	1.086/1.084	C <sub>3</sub> -C <sub>4</sub> - C <sub>5</sub> (120.4)	119.2	119.0/119.0	C <sub>10</sub> -C <sub>2</sub> -C <sub>3</sub> -H <sub>8</sub>	0.01	0.0/0.0
C <sub>5</sub> -C <sub>6</sub>	1.390	1.402/1.398	C <sub>3</sub> -C <sub>4</sub> -H <sub>7</sub>	120.3	120.4/120.4	N <sub>1</sub> -C <sub>2</sub> -C <sub>10</sub> -H <sub>11</sub>	59.13	58.96/58.93
C <sub>5</sub> -H <sub>9</sub> (0.960)	1.074	1.085/1.083	C <sub>5</sub> -C <sub>4</sub> -H <sub>7</sub>	120.3	120.4/120.4	N <sub>1</sub> -C <sub>2</sub> -C <sub>10</sub> -H <sub>12</sub>	- 179.9	-179.9/-179.9
C <sub>6</sub> -C <sub>14</sub>	1.506	1.508/1.507	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	118.4	118.7/118.7	N <sub>1</sub> -C <sub>2</sub> -C <sub>10</sub> -H <sub>13</sub>	- 59.12	-58.92/-58.9
C <sub>10</sub> -H <sub>11</sub> (1.093)	1.084	1.093/1.093	C <sub>4</sub> -C <sub>5</sub> -H <sub>9</sub>	121.0	120.9/120.9	C <sub>3</sub> -C <sub>2</sub> -C <sub>10</sub> -H <sub>11</sub>	- 120.8	-121.0/-121.0
C <sub>10</sub> -H <sub>12</sub> (1.070)	1.083	1.095/1.091	C <sub>6</sub> -C <sub>5</sub> -H <sub>9</sub>	120.5	120.2/120.2	C <sub>3</sub> -C <sub>2</sub> -C <sub>10</sub> -H <sub>12</sub>	-0.01	-0.0/-0.0
C <sub>10</sub> -H <sub>13</sub> (1.093)	1.084	1.095/1.093	N <sub>1</sub> -C <sub>6</sub> -C <sub>5</sub>	122.0	121.9/121.9	C <sub>3</sub> -C <sub>2</sub> -C <sub>10</sub> -H <sub>13</sub>	120.8	121.0/121.0
C <sub>14</sub> -H <sub>15</sub> (1.093)	1.084	1.095/1.093	N <sub>1</sub> -C <sub>6</sub> -H <sub>14</sub>	116.2	116.3/116.3	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	0.01	0.0/0.0
C <sub>14</sub> -H <sub>16</sub> (1.070)	1.084	1.093/1.093	C <sub>5</sub> -C <sub>6</sub> -H <sub>14</sub>	121.7	121.7/121.7	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> -H <sub>7</sub>	- 179.9	180.0/180.0
C <sub>14</sub> -H <sub>17</sub> (1.093)	1.083	1.095/1.091	C <sub>2</sub> -C <sub>10</sub> - H <sub>11</sub> (111.0)	109.9	111.7/111.7	H <sub>8</sub> -C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	179.9	180.0/180.0
-	-	-	C <sub>2</sub> -C <sub>10</sub> - H <sub>12</sub> (111.7)	111.6	110.2/110.2	H <sub>8</sub> -C <sub>3</sub> -C <sub>4</sub> -H <sub>7</sub>	-0.01	0.0/0.0
-	-	-	C <sub>2</sub> -C <sub>10</sub> -H <sub>13</sub>	109.9	110.2/110.2	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	0.01	0.0/0.0
-	-	-	H <sub>11</sub> -C <sub>10</sub> -H <sub>12</sub>	108.7	108.6/108.6	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> -H <sub>9</sub>	179.9	180.0/180.0
-	-	-	H <sub>11</sub> -C <sub>10</sub> -H <sub>13</sub>	107.5	108.6/108.6	H <sub>7</sub> -C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	- 179.9	180.0/180.0
-	-	-	C <sub>12</sub> -C <sub>10</sub> -H <sub>13</sub>	108.7	107.0/107.0	H <sub>7</sub> -C <sub>4</sub> -C <sub>5</sub> -H <sub>9</sub>	- 0.004	0.0/0.0
-	-	-	C <sub>6</sub> -C <sub>14</sub> - H <sub>15</sub> (111.0)	109.9	110.2/110.2	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub> -N <sub>1</sub>	-0.02	-0.0/0.0
-	-	-	C <sub>6</sub> -C <sub>14</sub> - H <sub>16</sub> (106.0)	109.9	111.7/111.7	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub> -H <sub>14</sub>	180.0	-179.92/- 179.99
-	-	-	C <sub>6</sub> -C <sub>14</sub> -H <sub>17</sub>	111.6	110.2/110.2	H <sub>9</sub> -C <sub>5</sub> -C <sub>6</sub> -N <sub>1</sub>	179.9	-180/-180.0
-	-	-	H <sub>15</sub> -C <sub>14</sub> -H <sub>16</sub>	107.5	108.6/108.6	H <sub>9</sub> -C <sub>5</sub> -C <sub>6</sub> -H <sub>14</sub>	0.01	0.0/0.0
-	-	-	H <sub>15</sub> -C <sub>14</sub> -H <sub>17</sub>	108.7	107.0/107.0	N <sub>1</sub> -C <sub>6</sub> -C <sub>14</sub> -H <sub>15</sub>	- 59.12	-58.93/-58.91
-	-	-	H <sub>16</sub> -C <sub>14</sub> -H <sub>17</sub>	108.7	108.6/108.6	N <sub>1</sub> -C <sub>6</sub> -C <sub>14</sub> -H <sub>16</sub>	59.13	58.9/58.9
-	-	-	-	-	-	N <sub>1</sub> -C <sub>6</sub> -C <sub>14</sub> -H <sub>17</sub>	- 179.9	179.9/179.9
-	-	-	-	-	-	C <sub>5</sub> -C <sub>6</sub> -C <sub>14</sub> - H <sub>15</sub>	120.8	121.0/121.0
-	-	-	-	-	-	C <sub>5</sub> -C <sub>6</sub> -C <sub>14</sub> -H <sub>16</sub>	- 120.8	-121.0/-121.0
-	-	-	-	-	-	C <sub>5</sub> -C <sub>6</sub> -C <sub>14</sub> -H <sub>17</sub>	-0.01	-0.001/-0.00



**Fig. 4.** Dihedral angle differences from theoretical (HF/DFT) approaches

The order of the optimized bond angles as  $C2-C3-C4=C4-C5-C6 < C1-N1-C6=C3-C4-C5 < C1-C6-C5=N1-C2-C3$ . The pyridine ring of title molecule appears a little distorted with  $C2-N-C6$  bond angle  $119.4^\circ$ , by B3LYP/6-311++G (d, p) exactly at the substitution and rest to the substitution place longer than  $C3-C4-C5$  bond angle  $119.0^\circ$  by same method. In this case B3LYP method leads to geometric parameters which are much closer to experimental data. Because of these reasons we take into account B3LYP/6-31++G (d, p) and 6-311++G (d, p) levels of vibrational analysis for present discussion.

#### 4. 2. Vibrational assignments

The 2,6Ltn consists of 17 atoms, and belongs to  $C_{2v}$  symmetry. Hence the number of normal modes of vibrations for 2,6Ltn works to 45. Of the 45 normal modes of vibrations, 15 modes of vibrations are stretching, 14 modes of vibrations are in-plane bending and 16 modes of vibrations are out-of-plane bending. Thus the 45 normal modes of vibrations title molecule are distributed among the symmetry species are

$$\Gamma \text{ Vib} = 15A_1 + 7A_2 + 9B_1 + 14B_2$$

The bands that belong to stretching modes are represented as  $A_1$  and  $B_2$ , while ring deformation, in-plane bending vibrations and corresponds to ring, torsion and out of plane

bending modes as  $A_2$  and  $B_1$ . The harmonic-vibrational frequencies calculated for 2,6Ltn at HF and B3LYP levels using the triple split valence basis set along with the diffuse and polarization functions, 6-31+G (d, p), 6-31++G (d, p) and 6-311++G (d, p) observed FT-IR and FT-Raman frequencies for various modes of vibrations have been presented in the table 2. Comparison of frequencies calculated at HF and B3LYP with the experimental values reveals the over estimation of the calculated vibrational modes due to the neglect of anharmonicity in real system.

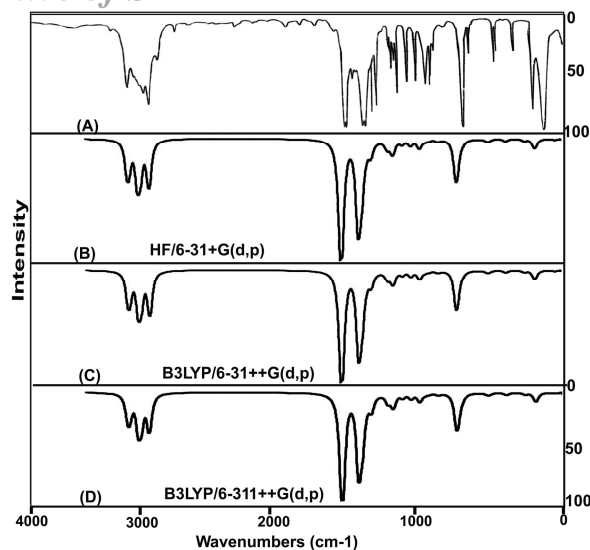
Inclusion of electron correlation in the Density functional theory to certain extends makes the frequency values smaller in the comparison with the HF frequency data. The comparative FTIR and FTRaman graphs of observed and computed for three sets are presented in the Figs. 5 & 6. Reduction in the computed harmonic vibrations, although basis set sensitive are only marginal as observed in the DFT values using 6-311++G (d, p). The scaled calculated frequencies minimize the root-mean square difference between calculated and experimental frequencies for bands with definite identifications.

#### 4. 2. 1. Computed IR Intensity and Raman Activity Analysis

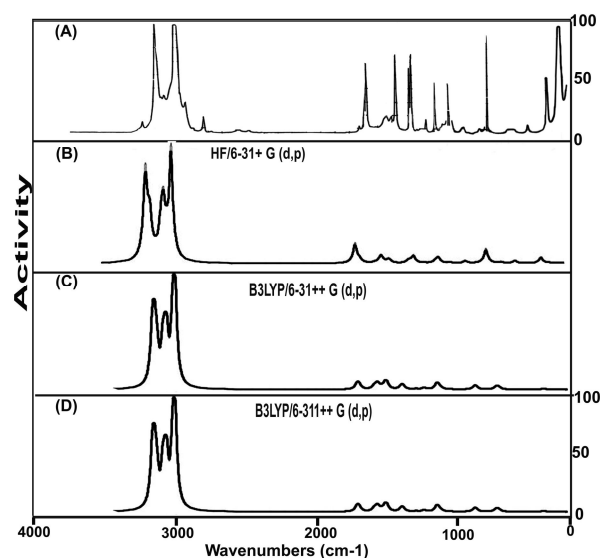
Computed vibrational spectral IR intensities and Raman activities of the 2,6Ltn for corresponding wave numbers by HF and DFT methods with B3LYP at 6-31+G (d, p), 6-31++G (d, p) and 6-311++G (d, p) basis sets are given in the Table 3. Comparison of IR intensity and Raman activity calculated by HF and DFT with B3LYP at 6-31+G (d, p), 6-31++G (d, p) and 6-311++G (d, p) methods with experimental values shows the variation of IR intensities and Raman activities. In the case of IR intensity, the values of HF at 6-31+G (d, P) level are found to be higher than B3LYP/ at 6-31++G (d, P) and 6-311++G (d, P) whereas in the case of Raman activity the effect is reversed. The similar effect was also noticed in the earlier paper [32].

**Table 2.** Observed and HF /6-31+ G (d, p), B3LYP/6-31++G (d, p) and B3LYP/6-311++G (d, p) level calculated vibrational frequencies of 2, 6-Lutidine

S.No.	Symmetry Species C <sub>2v</sub>	Observed Frequency	Calculated Frequency (cm <sup>-1</sup> ) with HF/6-31+G(d, p)	Calculated Frequency (cm <sup>-1</sup> ) with B3LYP/6-31++G (d, p) Unscaled Value	Calculated Frequency (cm <sup>-1</sup> ) with B3LYP/6-311++G (d, p) scaled Value	Vibrational Assignments	S.No	Symmetry Species C <sub>2v</sub>	Observed Frequency	Calculated Frequency (cm <sup>-1</sup> ) with HF/6-31+G (d, p)
		FTIR	FTRaman			Unscaled Value	scaled Value	Unscaled Value	scaled Value	
1	A <sub>1</sub>	3070vs	3070vs	3376	3058	3205	3070	3188	3050	(C-H) v
2	A <sub>1</sub>	-	3030s	3368	3051	3197	3027	3180	3043	(C-H) v
3	A <sub>1</sub>	3020m	-	3346	3031	3181	3012	3163	3026	(C-H) v
4	B <sub>2</sub>	2960vs	-	3270	2962	3128	2962	3110	2970	(C-H) (CH <sub>3</sub> )
5	B <sub>2</sub>	2950vs	-	3269	2961	3127	2961	3110	2970	(C-H) v (CH <sub>3</sub> )
6	B <sub>2</sub>	-	2940vs	3258	2951	3107	2942	3089	2949	(C-H) v (CH <sub>3</sub> )
7	B <sub>2</sub>	-	2930vs	3258	2951	3107	2942	3089	2949	(C-H) v (CH <sub>3</sub> )
8	B <sub>2</sub>	-	2910vs	3194	2893	3045	2908	3033	2896	(C-H) v (CH <sub>3</sub> )
9	B <sub>2</sub>	2860s	-	3193	2892	3044	2907	3032	2895	(C-H) v (CH <sub>3</sub> )
10	A <sub>1</sub>	1600s	1600vs	1785	1617	1634	1601	1626	1606	(C=C) v
11	A <sub>1</sub>	1590vs	-	1783	1615	1627	1594	1617	1597	(C=C) v
12	A <sub>1</sub>	1510vs	-	1628	1474	1504	1500	1500	1482	(C=N) ã (C-C) v
13	A <sub>1</sub>	1500m	-	1626	1473	1502	1498	1498	1480	(C-C) v
14	A <sub>1</sub>	1470vs	-	1601	1450	1481	1478	1477	1459	(CH <sub>3</sub> ) α
15	A <sub>1</sub>	1460vs	-	1600	1449	1480	1477	1476	1458	(CH <sub>3</sub> ) α
16	B <sub>2</sub>	1450vs	1450w	1600	1449	1478	1475	1473	1455	(CH <sub>3</sub> ) α
17	B <sub>2</sub>	1440vs	1440w	1585	1436	1448	1445	1442	1424	(CH <sub>3</sub> ) α
18	A <sub>1</sub>	-	1420w	1542	1397	1414	1411	1409	1392	(CH <sub>3</sub> ) α
19	A <sub>1</sub>	-	1400w	1541	1396	1413	1410	1408	1391	(CH <sub>3</sub> ) α
20	B <sub>2</sub>	1260vs	1260vs	1387	1256	1304	1259	1287	1271	(C-H) δ (C-N) v
21	A <sub>1</sub>	1240vs	-	1358	1230	1289	1245	1285	1256	(C-H) δ (C-CH <sub>3</sub> ) v
22	A <sub>1</sub>	1160vs	1160w	1319	1195	1252	1160	1249	1221	(C-H) δ
23	A <sub>1</sub>	1100vs	1100vs	1206	1092	1183	1096	1179	1131	(C-H) δ (CH <sub>3</sub> )
24	A <sub>1</sub>	1095vs	1095vs	1203	1090	1120	1094	1117	1072	(C-H) δ (CH <sub>3</sub> )
25	B <sub>2</sub>	-	1050w	1164	1054	1063	1038	1061	1049	(C-H) δ (CH <sub>3</sub> )
26	B <sub>2</sub>	-	1040w	1157	1048	1056	1031	1055	1043	(C-H) δ (CH <sub>3</sub> )
27	B <sub>2</sub>	1030vs	-	1124	1014	1052	1027	1050	1038	(C-H) δ (CH <sub>3</sub> )
28	B <sub>2</sub>	1000vs	1000vs	1122	1016	1018	997	1018	1006	(C-H) δ (CH <sub>3</sub> )
29	A <sub>2</sub>	995s	-	1100	996	1003	982	1001	990	(C-H) γ
30	A <sub>2</sub>	980m	-	1075	974	988	968	988	977	(C-H) γ
31	A <sub>2</sub>	900w	-	988	895	920	901	918	907	(C-H) γ
32	B <sub>1</sub>	880w	880w	982	889	898	880	897	887	(C-H) γ (CH <sub>3</sub> )
33	B <sub>1</sub>	770vs	770vs	863	782	783	767	782	773	(C-H) γ (CH <sub>3</sub> )
34	A <sub>2</sub>	730m	-	814	737	745	730	748	739	(C-H) γ (CH <sub>3</sub> )
35	B <sub>1</sub>	710m	-	775	702	727	712	727	719	(C-H) γ (CH <sub>3</sub> )
36	B <sub>2</sub>	560m	560m	620	561	567	555	565	558	(CCC) δ
37	B <sub>2</sub>	-	540m	600	543	561	549	562	555	(CCC) δ
38	B <sub>2</sub>	530m	-	581	526	544	533	544	538	(C-N-C) δ
39	A <sub>2</sub>	-	430m	483	437	440	431	440	435	(CCC) γ
40	A <sub>2</sub>	410s	-	451	408	422	413	420	415	(CCC) γ
41	B <sub>1</sub>	290vs	290vs	301	272	282	276	281	278	(C-CH <sub>3</sub> ) γ
42	B <sub>1</sub>	210vs	210vs	225	203	207	202	206	203	(C-N-C) γ
43	A <sub>2</sub>	-	200vs	223	202	198	194	195	193	(CH <sub>3</sub> ) τ



**Fig. 5.** Experimental (A), calculated (B), (C) & (D) FTIR spectra of 2,6-Lutidine



**Fig. 6.** Experimental (A), calculated (B), (C) & (D) FT-Raman spectra of 2,6-Lutidine

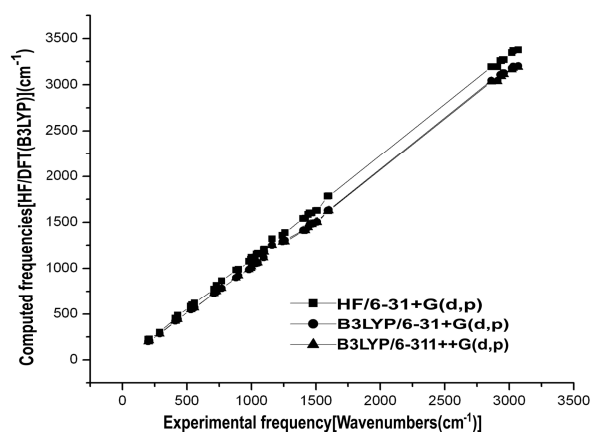
#### 4. 2. 2. Computed Vibrational frequency Analysis

The comparative graph of calculated vibrational frequencies by HF and DFT methods (B3LYP) at 6-31+G (d, p), 6-31++G (d, p) and 6-311++G (d, p) basis sets for the 2,6Ltn are given in the Fig. 7. From the figure, it is found that the calculated (unscaled) frequencies by B3LYP with 6-31++G (d, p) and 6-311++G (d, p) basis sets are closer to the experimental frequencies. This observation is in line with our earlier work [18]. The standard deviation (SD) calculation made between experimental and

computed frequencies DFT for the 2,6Ltn is presented in the table. 4. According to the SD, the computed frequency deviation decreases in going from HF to B3LYP/6-31++G (d, p) to B3LYP/6-311++G (d, p). The deviation ratio between HF/6-31+G (d, p) and B3LYP/6-31++G (d, p) is 2.90 and HF/6-31+G (d, p) and B3LYP/6-311++G (d, p) is 3.23. It is also observed that the calculated frequencies by B3LYP/6-311++G (d, p) basis sets are closer to the experimental frequencies than other basis sets in DFT method.

#### 4. 2. 3. C-H Vibrations

The presence of C-H vibrations in the region 3000-3100  $\text{cm}^{-1}$  confirms the molecule to be hetero aromatic [33-35]. In this case, the bands are observed at 3070, 3030 and 3020  $\text{cm}^{-1}$  for aromatic C-H stretching vibrations. The theoretically computed for C-H vibrations by B3LYP/6-31++G (d, p) and B3LYP/6-311++G (d, p) methods shows good agreement with recorded spectrum as well as literature data. The in-plane and out-of-plane bending vibrations of these C-H generally lies in the range 1000 - 1300  $\text{cm}^{-1}$  and 950 - 800  $\text{cm}^{-1}$  respectively [36-38]. In 2,6Ltn, the bands at 1260, 1240 and 1160  $\text{cm}^{-1}$  have been observed for the C-H in-plane bending and the bands appeared at 995, 980 and 900  $\text{cm}^{-1}$  for C-H out-of-plane bending. According to the literature, these assignments are found in the expected range which indicates the substitutions do not affect much the vibration of aromatic C-H.



**Fig. 7.** Comparative graph of experimental and computed frequencies [HF/DFT(B3LYP)]

**Table 3.** Comparative values of IR intensities and Raman Activities between HF/6-31+G (d, p), B3LYP/6-31++G (d, p) and B3LYP/6-311++ G (d, p) of 2, 6-Lutidine

S.No.	Calculated with HF/6-31+G (d, p)			Calculated with B3LYP/6-31++G (d, p)			Calculated with B3LYP/6-311++G (d, p)		
	Scaled Frequency	IR Intensity (Ai)	Raman Activity (I)	Scaled Frequency	IR Intensity (Ai)	Raman Activity (I)	Scaled Frequency	IR Intensity (Ai)	Raman Activity (I)
1	3058	16.78	175.69	3070	14.36	225.52	3050	12.64	179.30
2	3051	24.77	54.43	3027	22.32	71.68	3043	20.18	51.89
3	3031	9.10	75.07	3012	4.02	84.22	3026	3.63	72.95
4	2962	27.34	77.66	2962	14.93	68.50	2970	14.78	117.40
5	2961	26.39	50.50	2961	21.23	57.69	2970	19.89	0.01
6	2951	42.51	148.51	2942	22.99	137.25	2949	23.06	148.51
7	2951	0.00	25.85	2942	0.00	37.25	2949	0.00	0.00
8	2893	12.24	268.70	2908	9.55	406.74	2896	8.09	287.35
9	2892	39.05	7.45	2907	33.23	30.22	2895	30.29	2.80
10	1617	85.54	7.91	1601	46.39	9.71	1606	47.81	23.64
11	1615	105.10	22.37	1594	74.56	21.04	1597	74.69	8.57
12	1474	15.01	13.21	1500	60.94	0.84	1482	59.96	12.26
13	1473	56.31	0.11	1498	16.57	8.12	1480	17.21	0.37
14	1450	0.00	37.02	1478	0.00	18.11	1459	0.00	29.42
15	1449	7.94	0.18	1477	15.09	0.16	1458	14.96	8.25
16	1449	18.42	0.97	1475	18.34	3.04	1455	22.77	2.44
17	1436	3.41	10.80	1445	2.13	6.13	1424	2.13	19.07
18	1397	1.33	16.23	1411	8.58	18.89	1392	9.33	9.55
19	1396	0.70	9.68	1410	3.53	13.60	1391	4.68	6.62
20	1256	6.71	4.58	1259	1.04	0.06	1271	6.98	3.39
21	1230	17.83	1.15	1245	6.88	19.61	1256	1.56	0.57
22	1195	0.06	2.03	1160	13.46	0.04	1221	13.81	2.92
23	1092	2.34	4.72	1096	3.95	2.26	1131	4.20	0.26
24	1090	20.24	0.25	1094	5.44	5.69	1072	5.45	6.27
25	1054	0.00	0.93	1038	0.00	0.02	1049	0.00	1.00
26	1048	11.13	0.20	1031	8.40	0.02	1043	8.50	0.64
27	1014	3.58	0.02	1027	0.08	0.04	1038	0.06	0.64
28	1016	0.52	0.59	997	1.24	25.43	1006	1.25	0.62
29	996	0.61	16.78	982	0.03	0.02	990	0.01	9.64
30	974	3.95	7.56	968	1.02	3.11	977	0.86	14.19
31	895	0.00	0.77	901	1.84	0.01	907	1.84	1.20
32	889	0.26	0.71	880	0.0	0.50	887	0.00	0.27
33	782	44.84	0.59	767	41.29	0.32	773	40.23	0.42
34	737	1.09	0.97	730	1.36	0.15	739	3.00	1.04
35	702	0.69	16.16	712	0.55	15.68	719	0.55	16.31
36	561	0.00	0.28	555	0.00	1.28	558	0.00	0.39
37	543	2.91	9.19	549	1.43	10.5	555	1.39	9.59
38	526	2.99	5.74	533	1.75	4.92	538	1.71	5.19
39	437	0.00	1.12	431	0.00	0.32	435	0.00	0.77
40	408	2.51	0.19	413	2.26	0.16	415	2.36	0.40
41	272	1.63	0.65	276	1.80	1.13	278	1.79	0.29
42	203	8.60	1.13	202	9.46	0.51	203	9.40	1.77
43	202	0.00	4.33	194	0.00	2.66	193	0.00	3.73

**Table 4.** Standard Deviation of frequencies Computed by HF/DFT (B3LYP) at 6-31++G (d, p) and 6-311++G (d, p) basis sets

S.No.	Basic set levels	Total values	Average	Standard Deviation Average	Deviation ratio
	Experimental	60620	1409.76		
1	HF/6-31+(d, p)	66944	1556.83	103.99	
5	B3LYP/6-31++(d, p)	62744	1459.16	35.75	2.90
6	B3LYP/6-311++(d, p)	62495	1453.37	32.18	3.23



#### 4. 2. 4. Methyl group vibrations

Residual alkane groups are found in a very large number of compounds and hence are an extremely important class [39]. Four types of vibration are normally observed, namely stretching and deformation of C-H and C-C bonds. The C-H vibration frequencies of methyl and methylene groups fall in narrow ranges of saturated hydrocarbons. However, atoms directly attached to  $-\text{CH}_3-$  may result in relatively large shifts in the absorption frequencies. In general, the effect of electronegative groups or atoms is to increase the C-H absorption frequency.

The 2,6Ltn possesses two  $\text{CH}_3$  groups in second and sixth position of the ring. The C-H stretching of the methyl groups are highly localized and generally observed in the range  $3000 - 2900 \text{ cm}^{-1}$  [40-43]. In the present molecule, the bands with sharp peaks found at 2960, 2950, 2940, 2930, 2910 and  $2860 \text{ cm}^{-1}$  have been assigned to C-H stretching vibrations for methyl. All the observed stretching vibrations are in the expected range and agree well with the earlier work. This is strongly proving the substitutions of methyl groups in the ring. The C-H in-plane bending vibrations are identified at 1095, 1050, 1040 and  $1000 \text{ cm}^{-1}$  for 2,6Ltn and the C-H out-of-plane bending vibrations are found at 880, 770, 730, and  $710 \text{ cm}^{-1}$ . These assigned frequencies are in good agreement with those found for aromatic C-H modes [44-50]. These observations showed that the methyl group vibrations not much influenced by the inclusion of N in the ring.

#### 4. 2. 5. C-C Vibrations

The theoretically computed frequencies by B3LYP/6-31++G (d, p) and B3LYP/6-311++G (d, p) methods are assigned for C=C and C-C stretching vibrations nearly coincides with FTIR and FTRaman spectra. The C-C stretching vibration is very much prominent in the spectrum of pyridine and its derivation and is highly characteristic of the aromatic ring itself [51]. The C-C stretching vibrations are normally found at  $1400 - 1650 \text{ cm}^{-1}$  in benzene

derivatives [52-54]. In this case, two bands are observed at 1600 and  $1590 \text{ cm}^{-1}$  for C=C stretching vibrations and two strong bands observed at  $1510 \text{ cm}^{-1}$  and  $1500 \text{ cm}^{-1}$  assigned to C-C stretching vibrations. These assignments agree well with the literature values. The CCC bending bands always occur below  $600 \text{ cm}^{-1}$  [55]. In 2,6Ltn, the bands at 560 and  $540 \text{ cm}^{-1}$  are assigned to CCC in-plane bending vibrations. Two supplementary bands observed at 430 and  $410 \text{ cm}^{-1}$  for CCC out-of-plane bending vibrations. These assignments are in line with the assignments proposed by the above literature.

#### 4. 2. 6. C-N Vibrations

The Pyridine show a strong absorption band in the region  $1600 - 1500 \text{ cm}^{-1}$  due to the C=N ring stretching vibrations [56]. Accordingly, a strong band is observed at  $1510 \text{ cm}^{-1}$  for the C=N ring stretching vibration. A small change in frequency observed for this mode is mainly due to the presence of methyl groups attached with ring and also coupled with C-C vibration. The C-N stretching vibration is always mixed with other bands and regularly assigned in the region  $1382 - 1266 \text{ cm}^{-1}$  [57-59]. In this investigation, a C-N stretching band is observed strongly at  $1260 \text{ cm}^{-1}$ . This frequency is also at the lower end of the expected range which is purely due to the interaction of methyl group attached with C in the ring and is also lie in the region of C-H bending vibration. This view is supported by the literature [60]. The C-N in-plane bending vibration assigned at  $530 \text{ cm}^{-1}$  and the C-N out-of-plane bending vibration found at  $210 \text{ cm}^{-1}$ . These assignments are in line with the literature [61].

#### 4. 2. 7. C-CH<sub>3</sub> and CH<sub>3</sub> vibrations

In this investigation, the methyl deformation,  $(\text{CH}_3) \delta$  found at 1470, 1460, 1450, 1440, 1430 and  $1400 \text{ cm}^{-1}$ . This assignment is supported by the literature [62-64]. According to the literature, these observed frequencies lie in the asymmetrical region which is purely due to the coupling of methyl

groups with the ring. The IR band for C-CH<sub>3</sub> stretching vibration identified at 1240 cm<sup>-1</sup>. This assignment supported by the literature [65]. The theoretically computed values by B3LYP/6-31++G (d, p) and B3LYP/6-311++G (d, p) methods for C-H deformations are scaled down and are nearly coincides with FTIR experimental values.

The bands at 290 and 200 cm<sup>-1</sup> are observed for C-CH<sub>3</sub> out-of-plane bending and CH<sub>3</sub> twisting vibrations respectively. According to the literature [66], these vibrations are slightly deviated down, which may be due to the presence of C=N and C-N bonds in the ring.

## 5. Conclusions

The FTIR and FTRaman spectra have been recorded and the detailed vibrational assignments are done for 2, 6-Lutidine. The equilibrium geometries, harmonic vibrational frequencies, FTIR and FTRaman spectra of the title molecule are analyzed by ab-initio HF and DFT calculations with HF/6-31+G (d, p), B3LYP/6-31++G (d, p) and B3LYP/6-311++G (d, p) basis sets. The difference between calculated and experimental frequencies is very small for most of the fundamentals. Therefore the results presented in this work for 2,6Ltn indicate that DFT method of quantum mechanical calculations is reliable for prediction of both FTIR and FTRaman spectra of the title compound. Even the substitutions of methyl groups symmetrically in the heterocyclic ring, the ring C-H stretching bands are not affected and are observed with strong or very strong intensity. Out of the 45 normal modes of vibrations, only 42 vibrations could be assigned since the last three are below the observed range.

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