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# Vibrational spectroscopy (FTIR and FTRaman) investigation using DFT analysis on the Structure of 2-chloro-5-nitropyridine

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**Abstract.** This work deals with vibrational spectroscopy of 2-chloro-5-nitropyridine by means of quantum chemical calculations. The Fourier transform infrared (FT-IR) and FT-Raman spectra of CNP have been measured in the range 4000–50 $\mathrm{cm}^{-1}$ and 3500–50 $\mathrm{cm}^{-1}$ respectively. Complete vibrational assignments and analysis of the fundamental modes of the compound are carried out using the observed FT-IR and FT-Raman data. The geometry is optimized without any symmetry constraints using the DFT/B3LYP method with 6-311++G basis set. The vibrational frequencies which were determined experimentally are compared with those obtained theoretically from density functional theory (DFT) gradient calculations for the optimized geometry of the compound. The structural parameters and normal modes of vibrations obtained from DFT method are in good agreement with experimental data.

**Keywords**: 2-chloro-5-nitropyridine; Gaussian-09; DFT, FT-IR, FT-Raman, Vibrational assignment.

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# 1 Introduction

Pyridine is a biologically important heterocyclic aromatic compound having penetrating odour and serving as the parent compound of many biologically important derivatives. Pyridine include compounds used as water repellants, herbicides, insecticides, pharmaceuticals, food flavourings, dyes, rubber chemicals, adhesives, paints, explosives and disinfectants [26]. Vibrational spectra of substituted pyridine received considerable attention in the spectroscopic view of their obvious importance to biological systems and industrial significance [14, 17, 23].

Measurements of integrated intensities of the observed absorption bands and theoretical normal coordinate analysis using abinitio methods give information regarding the nature of functional groups, orbital interactions and mixing of skeletal frequencies. Hence, the investigation on the structure and fundamental vibrations of pyridine and its derivatives are still being carried out [8, 11, 24].

The position of the substituents in the pyridine ring as well as its electron donor/acceptor capabilities play very important role on the structural and electronic properties of the molecules. Extensive recent studies on vibrational spectra of substituted pyridines assigned complete vibrational mode and frequency analysis [9, 11, 18]. Vibrational spectra of some halogeno pyridines were reported by Green et al [24]. They compared the assignment with that of halogen substituted benzenes and found to agree excellently. Following Green et al, many others reported the vibrational analysis of disubstituted pyridines. Tripathi recorded the spectra of disubstituted halogeno-pyridines in the frequency range 250–4000 cm$^{-1}$ and most of their assignments agree well with the literature values [11].

The laser Raman spectrum of 2-chloro-3-nitropyridine in the poly crystalline state has been reported by Sarma et al [19]. Assignments of some bands observed in the infra-red spectrum of 2-chloro-3,5-dinitropyridine is in literature [12] and these have been used for the comparison with the assignments made for the title compound.

In spite of recent studies on vibrational spectra of substituted pyridines, neither IR and Raman spectra nor the quantum mechanical calculations for 2-chloro-5-nitropyridine molecule have been reported, so far. Therefore, in the present work, the theoretical and experimental investigation of the vibrational spectra of this molecule have been undertaken.

## 2 Experimental

The fine crystalline sample was provided by Aldrich and used as such for the spectral measurements. The room temperature Fourier transform IR spectra of title compound was measured in the 4000–50 cm$^{-1}$ region at a resolution of $\pm 2$ cm$^{-1}$ using Brucker IFS 66V Fourier transform spectrometer equipped with an TGS detector, a KBr beam splitter and globar source. The far IR spectrum was recorded on the same instrument using polyethylene pellet technique. The FT Raman spectrum of CNP was recorded on the same instrument equipped with an FRA 106 FT-Raman accessory. The spectrum was recorded in the 3500–50 cm$^{-1}$ with Nd: YAG laser operating at 200 mW power. The reported wave numbers are expected to be accurate within $\pm 2$cm$^{-1}$.

# 3 Computational Details

Nowadays, quantum chemical methods provide powerful support for experimental structural studies. Therefore, molecular geometry, vibrational and some molecular properties have been studied by DFT method. The results of many studies have indicated that DFT is a powerful method for predicting the geometry and harmonic vibration of organic compounds [1, 10, 20]. Density Function theory DFT [15] with the hybrid functionals (B3LYP) [2, 15] and basis set 6-311++G [5] have been employed to calculate optimized bond lengths, bond angles, dihedral angles, atomic charge, vibrational frequencies with their IR intensities and Raman scattering activities. All these calculations are performed using Gaussian 09 Program [5] involving gradient geometry optimization on an Intel Core2Duo/2.20 GHz processor. The molecular structure of the title compound in the ground state was optimized by using DFT/B3LYP method with the standard 6-311++G basis set. The Cartesian representation of the theoretical force constants have been computed at optimized geometry by assuming Cs point group symmetry. The vibrational frequencies were also calculated with these methods. The assignment of the calculated wave numbers is aided by the animation option of the Gauss View 05 [10] graphical interface for Gaussian programs, which gives a visual presentation of the nature of the vibrational modes.

# 4 Result and Discussion

## 4.1 Molecular Geometry

The structure with the scheme of numbering the atoms of 2-chloro-5-nitropyridine is represented in Figure 1. The geometry of the molecule under investigation is considered by possessing cs point group symmetry. The 33 fundamental modes of vibrations of

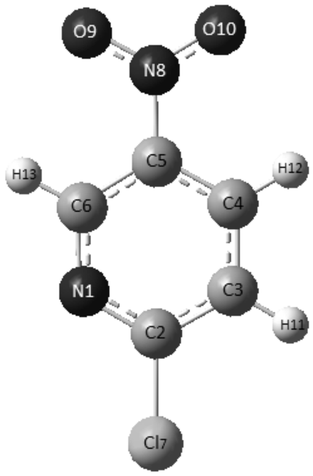

Figure 1: Structure of 2-chloro-5-nitropyridine along with numbering of atoms.

CNP are distributed into the irreducible representations under cs symmetry as 23 in-plane vibration of $A'$ species and 10 out-of-plane vibrations of $A''$ species.

$$\Gamma 3N-6 = 23A'(\text{in-plane}) + 10A''(\text{out-of-plane}).$$

All the vibrations are active in both IR and Raman. The observed FT-IR and simulated IR spectra of CNP are shown in the Figure 2. The FT-Raman spectra and its simulated counterpart are in Figure 3.

## 4.2 Structural properties

The molecular structure under study was optimized by using DFT/B3LYP method with the standard 6-311++G basis set. The optimized geometrical parameters of 2-chloro-5-nitro pyridine obtained by B3LYP/6-311++G density functional calculations is presented in Table 1.

Generally whenever there is substitution there are changes in the bond length of C─H bond due to change in the charge distribution between the carbon atoms of the

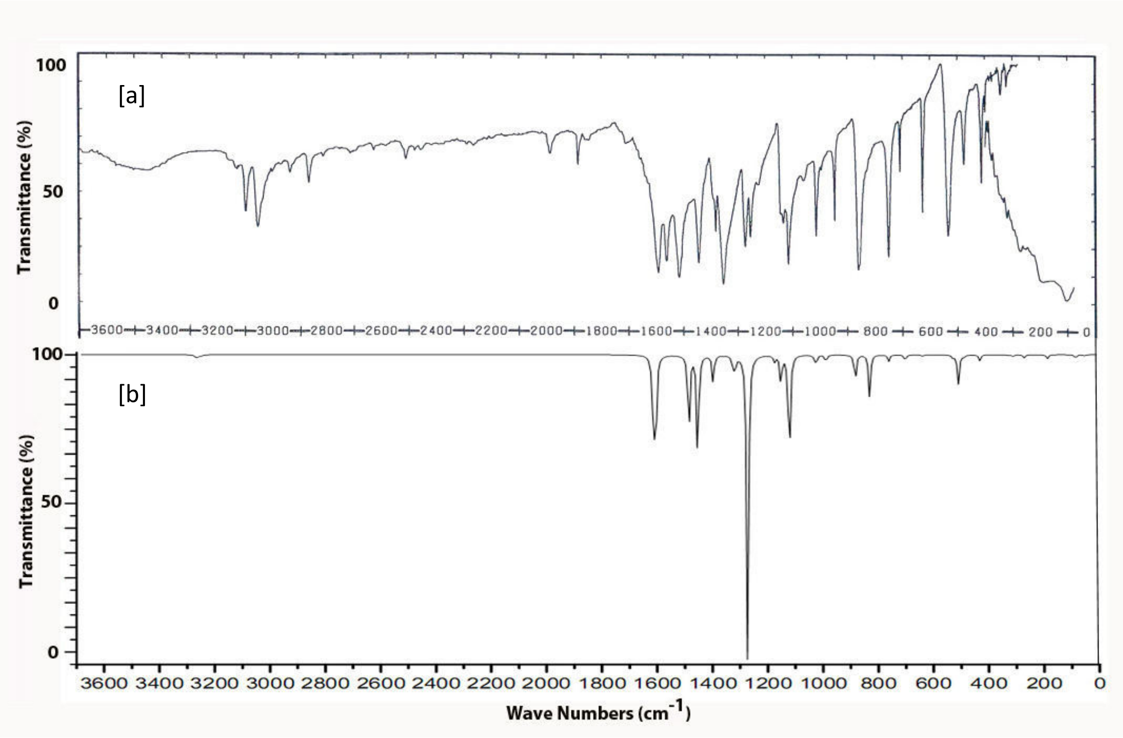

Figure 2: Comparison of observed and calculated infrared spectra of 2-chloro-5-nitropyridine. (a) Observed in solid phase. (b) Calculated with B3LYP/6-311++G.

pyridine ring. In the CNP molecule, the two substituents chloro and nitro groups are electron withdrawing in nature. The carbon atoms are bonded to the hydrogen atoms with a $\sigma$ bond in the pyridine ring and the substitution of chloro and nitro groups for hydrogen atoms increases the electron density at the ring carbon atoms by extensive conjugation. This is seen in the values reported in the literature [12] for the molecule 2-chloro-3,5-dinitro pyridine(CDNP).The values for the bond length of $C_2{-}C_{17}$ and $N_1{-}C_2$ values are higher in compound CDNP because there are two nitro groups in 3rd and 5th positions of the pyridine ring and therefore there is extended conjugation result-

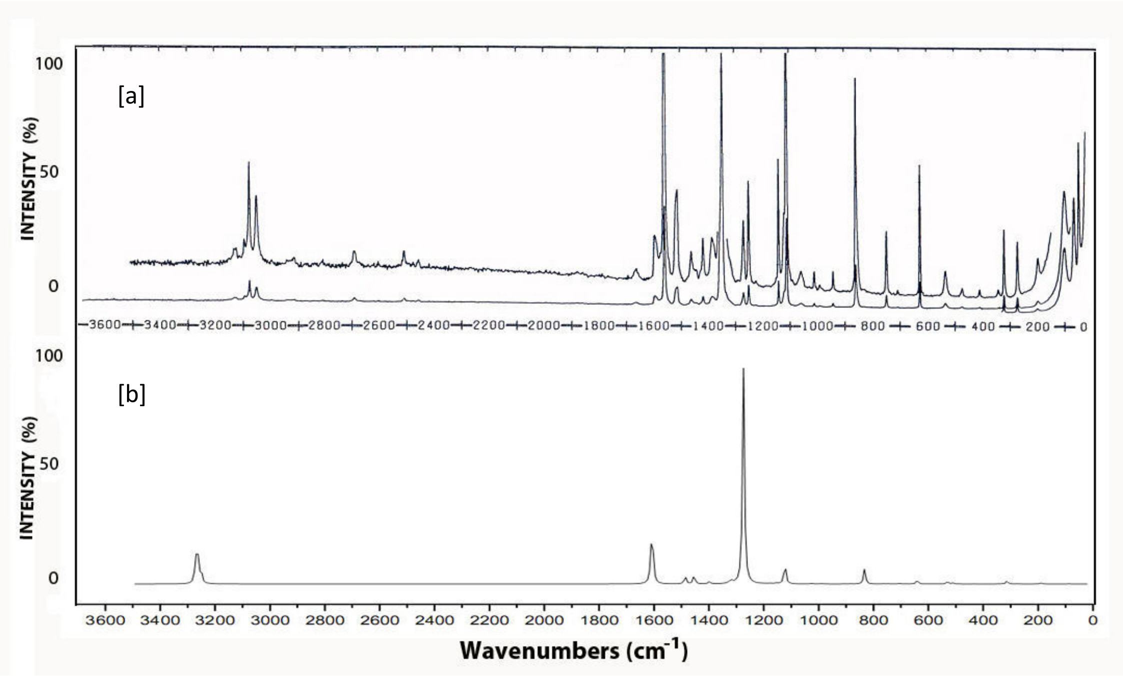

Figure 3: Comparison of observed and calculated Raman spectra of 2-chloro-5-nitropyridine. (a) Observed in solid phase. (b) Calculated with B3LYP/6-311++G.

ing in more double bond character for the $N_1{-}C_2$; $C_2{-}C_3$; $C_3{-}C_4$; $C_4{-}C_5$; $C_6{-}N_1$ and $C_2{-}C_{17}$. That is why in (CDNP) the bond length of all the ring atoms is less compared to bond length of ring atoms of the molecule CNP. In CNP, there is no that much of extended conjugation. This explanation is predicted by chemical principles which are in agreement with theoretical calculation (Table 1).

## 4.3 Assignment of Spectra

The Probable assignments of the title compound along with the observed and calculated frequencies and their relative intensities using B3LYP/6-311++G forcefield are

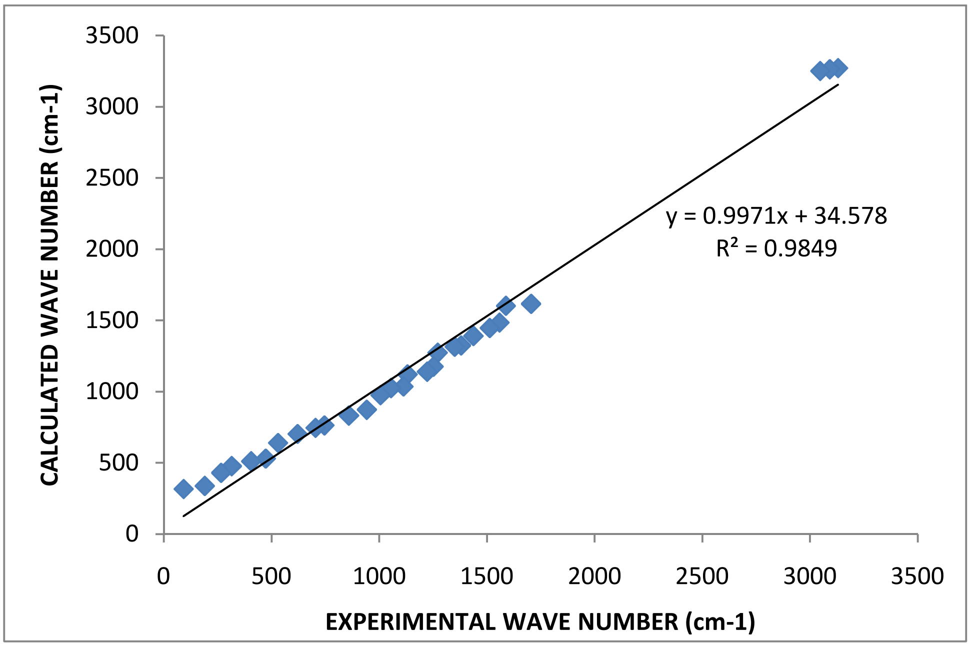

Figure 4: The correlation diagram for the calculated and the experimental frequencies of 2-chloro-5-Nitropyridine.

summarized in Table 2. The optimised structural parameters (Table 1) of the compound CNP is used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios.

The frequency values computed with DFT contain known systematic errors [4]. Better agreement between the computed and experimental frequencies can be obtained by using different scale factors for different regions of vibrations and it minimized the deviations very much between the computed and experimental frequencies at B3LYP/6-311++G calculation. The correlation diagram for the calculated and the experimental frequencies of CNP is shown in Figure 4.

### 4.3.1 Carbon Vibrations

Many ring modes are affected by the substitution to pyridine ring. Normally the bands between 1400–1650 cm$^{-1}$ in pyridine derivatives are assigned to C—C stretching modes [21]. Accordingly, in the present study, the pyridine ring of CNP compound, the ring absorbs strongly at 1437 and 1513 cm$^{-1}$ the FT-IR spectrum and at 1562 cm$^{-1}$ in the FT-Raman spectrum. The theoretically computed C—C stretching vibrations by B3LYP/6-311++G method at 1603 and 1302 cm$^{-1}$ shows good agreement with recorded spectrum as well as literature data.

The FT-IR bands at 1131, 621, 530 and 473 cm$^{-1}$ and FT-Raman bands at 641, 507 and 431 cm$^{-1}$ are assigned to C—C—C deformation of pyridine ring. The theoretically computed C—C—C deformation vibrations by B3LYP/6-311++G method at 1141, 641 and 318 cm$^{-1}$ shows good agreement with experimental values.

### 4.3.2 C—H Vibrations

The hetero aromatic structure shows the presence of C—H stretching vibrations in the region 3000–3100 cm$^{-1}$ which is the characteristic region for the ready identification of C—H stretching vibrations. This permits the ready identification of the structure. Further in this region, the bands are not affected due to the nature and position of the substituents nitro and chloro groups [25]. The calculated frequencies which lie in the range 3251, 3264 and 3271 cm$^{-1}$ are assigned to the three C—H stretching vibration of the title compound and their experimental counter part appear in the range 3047, 3092 and 3130 cm$^{-1}$ of IR spectrum. Thus, there is a good agreement between the experimental and calculated frequencies.

Generally, in the substituted pyridine, in-plane C—H bending appear in the range 1000–1300 cm$^{-1}$ and out-of-plane bending vibrations occur in the frequency range

750–1000 $cm^{-1}$ [3]. Accordingly, the calculated frequencies assigned to three C—H in-plane bending vibrations are in the region 1026–1392 $cm^{-1}$ while the observed IR frequencies are in the range 1055–1380 $cm^{-1}$. The calculated and observed frequencies assigned to three C—H out-of-plane bending vibrations are in the range 874–1177 $cm^{-1}$ and 859–942 $cm^{-1}$ respectively. The slight deviation in low frequency bands are due to the interactions between $NO_2$ and C—H out-of-plane bending frequencies [22].

### 4.3.3 C—N Vibrations

The presence of nitrogen in the ring of substituted pyridine structure gives rise to C—N stretching vibrations. Identification of these vibrations is rather difficult task as these vibrational frequency falls in the complicated region of the vibrational spectra. Generally, Nitro aromatic compounds show C—N stretching near 870 $cm^{-1}$ [7]. In the title compound, it was observed at 942 $cm^{-1}$ in IR spectrum which is in close agreement with theoretical values. The IR and Raman bands observed at 1131, 1252 and 1588 $cm^{-1}$ have been assigned to C—N stretching vibrations. The in-plane and out-of-plane bending vibrations assigned in the study are also supported by the literature [13].

## 4.4 Group Vibrations

### 4.4.1 $NO_2$ Group Vibrations

For a molecule with a $NO_2$ group, the $NO_2$ asymmetric stretching vibration band range is 1625–1540 $cm^{-1}$ and that of the symmetric stretching vibration is 1400–1360 $cm^{-1}$. The IR bands and Raman bands at 1271 and 1252 $cm^{-1}$ respectively with strong and medium intensity have been assigned to symmetric stretching. The IR and Raman bands observed at 1437, 1562, 1558 and 1588 $cm^{-1}$ have been assigned to asymmetric stretching [13]. Generally, Aromatic nitro compounds have a band of weak-to-medium intensity in region 590–300 $cm^{-1}$ due to the in-plane deformation mode of the $NO_2$ group [13]. This was observed at 530 $cm^{-1}$ in IR for the title compound and 531 $cm^{-1}$ in Raman spectrum. The out-of-plane $NO_2$ deformation vibrations have a weak-to-medium absorption in the region 775–662 $cm^{-1}$ [13]. For CNP, it was observed at 745 $cm^{-1}$ and 942 $cm^{-1}$ both in IR and Raman spectrum. The $NO_2$ torsional vibrations were observed at 266 and 189 $cm^{-1}$ in IR spectrum and at 270 and 195 $cm^{-1}$ in Raman spectrum. Also the calculated twisting $NO_2$ were identified at 96 and 59 $cm^{-1}$. As the torsional vibrations are very anharmonic; its frequency is difficult to reproduce within the harmonic region [16].

### 4.4.2 C—Cl Vibrations

The C—Cl stretching vibrations generally give strong bonds in the region 760–505 cm [13] Vibrational coupling with other groups may result in a shift in the absorption to as high as 840 $cm^{-1}$ [**?**]. Based on this, the FT-IR at 704 $cm^{-1}$ has been assigned to C—Cl stretching which is in close agreement with the theoretical calculation done by B3LYP/6-311++G which showed at 764 $cm^{-1}$ in IR band. Most of the aromatic chloro compounds have a band of strong to medium intensity in the region 385–265 $cm^{-1}$ due to C—Cl in-plane bending vibration [13]. Accordingly, the IR bands identified at 315 and 266 $cm^{-1}$ and Raman bands at 319 and 270 $cm^{-1}$ have been assigned to the C—Cl in-plane bending mode. The C—Cl out-of-plane deformation vibration has been established at 190 $cm^{-1}$ by IR and Raman spectrum. This is in close agreement with theoretical values shown in Table 2.

# 5 Conclusion

The molecular structural parameters and vibrational frequencies of the fundamental modes of the optimized geometry of CNP have been determined from DFT study. The geometry was optimized without any symmetric constraints using DFT/B3LYP with 6-311++G basis set. The complete vibrational analysis of the compound has been carried out The effects of substituents (Chloro & Nitro group) on vibrational frequencies were analysed. The computational results are in good agreement with experimental wave numbers.

Table 1: Optimized geometrical parameters of 2-cloro-5-nitropyridine obtained by B3LYP/6-311++G density functional calculations.

| Bond length | Value (Å) | Bond angle | Value ( ° ) | Dihedral angle | Value ( ° ) |
|---|---|---|---|---|---|
| $C_2$—$C_3$ | 1.4008 | A(3,2,1) | 124.682 | D(1,2,3,4) | 0 |
| $C_2$—$N_1$ | 1.33 | A(3,2,7 ) | 118.7254 | D(1,2,3,11) | 180 |
| $C_2$—$C_{17}$ | 1.809 | A(1,2,7) | 116.5926 | D(7,2,3,4) | 180 |
| $C_3$—$C_4$ | 1.394 | A(2,3,4) | 117.4087 | D(7,2,3,11) | 0 |
| $C_3$—H11 | 1.082 | A(2,3,11) | 121.042 | D(3,2,1,6) | 0 |
| $C_4$—$C_5$ | 1.4004 | A(4,3,11) | 121.5493 | D(7,2,1,6) | 180 |
| $C_4$—H12 | 1.0827 | A(3,4,5) | 118.1006 | D(2,3,4,5) | 0 |
| $C_5$—$C_6$ | 1.3971 | A(3,4,12) | 121.7692 | D(2,3,4,12) | 180 |
| $C_5$—$N_8$ | 1.4618 | A(5,4,12) | 120.1301 | D(11,3,4,5) | 180 |
| $C_6$—$N_1$ | 1.3507 | A(4,5,6) | 120.6274 | D(11,3,4,12) | 0 |
| $C_6$—H13 | 1.0809 | A(4,5,8) | 119.7114 | D(3,4,5,6) | 0 |
| $N_8$—$O_9$ | 1.2651 | A(6,5,8) | 119.6612 | D(3,4,5,8) | 180 |
| $N_8$—$O_{10}$ | 1.266 | A(5,6,1) | 120.8244 | D(12,4,5,6) | 180 |
| | | A(5,6,13) | 121.7969 | D(12,4,5,8) | 0 |
| | | A(1,6,13) | 117.3787 | D(4,5,6,1) | 0 |
| | | A(2,1,6) | 118.357 | D(4,5,6,13) | 180 |
| | | A(5,8,9) | 118.0618 | D(8,5,6,1) | 180 |
| | | A(5,8,10) | 118.0503 | D(8,5,6,13) | 0 |
| | | A(9,8,10) | 123.8879 | D(4,5,8,9) | 180 |
| | | | | D(4,5,8,10) | 0 |
| | | | | D(6,5,8,9) | 0 |
| | | | | D(6,5,8,10) | 180 |
| | | | | D(5,6,1,2) | 0 |
| | | | | D(12,6,1,2) | 180 |

Table 2: Detail assignments of fundamental vibrations of 2-chloro-5-nitro pyridine are summarized.

s-strong; vs-very strong; m-medium; w-weak; $\nu$a-asymmetric stretching; $\nu$s-symmetric stretching; $\beta$-in-plane bending; $\delta$-deformation; $\rho$-rocking; $\omega$-wagging; $\tau$-twisting; t-torsion; trigd-trigonal deformation; asymd-asymmetric deformation and symd-symmetric deformation.

| No. | Symmetry Species | Observed frequency (cm$^{-1}$) | | Calculated frequency (cm$^{-1}$) with B3LYP/6-311++G forcefield | | | | Assignment |
|---|---|---|---|---|---|---|---|---|
| | | FT-IR | FT-R | Unscaled | Scaled | IR | Raman | |
| 1 | $A'$ | 3130m | 3125w | 3271 | 3271 | 2.13 | 74.46 | $\nu$aCH |
| 2 | $A'$ | 3092s | 3090w | 3264 | 3264 | 3.13 | 96.58 | $\nu$sCH |
| 3 | $A'$ | 3047s | 3071s | 3251 | 3251 | 2.00 | 40.64 | $\nu$sCH |
| 4 | $A'$ | 1705m | 1562vs | 1617 | 1617 | 50.51 | 8.86 | $\nu$sCC + $\nu$sCN |
| 5 | $A'$ | 1588vs | 1509m | 1607 | 1603 | 141.78 | 139.15 | $\nu$sCC +($\nu$sNO + $\nu$sCN) |
| 6 | $A'$ | 1558s | 1455w | 1486 | 1486 | 97.60 | 17.22 | NO2 |
| 7 | $A'$ | 1513vs | 1418w | 1454 | 1447 | 136.11 | 18.37 | $\nu$aCC |
| 8 | $A'$ | 1437s | 1386w | 1399 | 1392 | 34.38 | 4.75 | $\nu$ CC |
| 9 | $A'$ | 1380s | 1251m | 1325 | 1325 | 19.26 | 4.31 | P NO2 |

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| No. | Symmetry Species | Observed frequency ($cm^{-1}$) | | Calculated frequency ($cm^{-1}$) with B3LYP/6-311++G forcefield | | | | Assignment |
|---|---|---|---|---|---|---|---|---|
| | | FT-IR | FT-R | Unscaled | Scaled | IR | Raman | |
| 10 | $A'$ | 1350vs | 1141s | 1316 | 1316 | 8.49 | 4.06 | $\nu$aCN +R asymd |
| 11 | $A'$ | 1271s | 1116vs | 1274 | 1274 | 356.85 | 435.85 | C−N |
| 12 | $A'$ | 1252s | 1059w | 1177 | 1177 | 7.40 | 0.70 | $5_C$h(sciss)+CN |
| 13 | $A'$ | 1222m | 1012w | 1153 | 1141 | 33.14 | 1.30 | C−H + C−N + CCl + $R_{asymd}$ |
| 14 | $A'$ | 1131s | 990w | 1123 | 1121 | 144.28 | 43.07 | $R_{symd}$ |
| 15 | $A''$ | 1112s | 940w | 1037 | 1037 | 1.17 | 0.10 | CC+CN |
| 16 | $A'$ | 1055m | 864vs | 1026 | 1026 | 12.48 | 1.45 | $b_{CH}$ + $b_{CC}$ |
| 17 | $A''$ | 1006s | 745m | 991 | 976 | 8.71 | 1.05 | *m*CH + $R_{trigd}$ |
| 18 | $A''$ | 942s | 628s | 885 | 874 | 34.47 | 0.37 | $CONO_2$ + CN |
| 19 | $A'$ | 859vs | 531w | 833 | 833 | 48.68 | 26.93 | $\nu$sCH |
| 20 | *A*” | 745s | 468w | 763 | 764 | 7.64 | 0.38 | Ring breathing |
| 21 | $A'$ | 704m | 405w | 747 | 747 | 0.14 | 0.55 | $\delta_R$ |

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| No. | Symmetry Species | Observed frequency (cm$^{-1}$) | | Calculated frequency (cm$^{-1}$) with B3LYP/6-311++G forcefield | | | | Assignment |
|---|---|---|---|---|---|---|---|---|
| | | FT-IR | FT-R | Unscaled | Scaled | IR | Raman | |
| 22 | $A''$ | 621s | 339w | 704 | 704 | 7.44 | 1.22 | CN+CC + $b_{CCl}$+$b_{CH}$ |
| 23 | $A'$ | 530s | 320m | 641 | 641 | 1.99 | 7.21 | 8$C_{CC}$(sciss) +5cnc(sciss) |
| 24 | $A'$ | 473m | 270w | 530 | 531 | 3.70 | 4.02 | $5_R$ |
| 25 | $A'$ | 405m | 195w | 512 | 512 | 35.49 | 1.52 | C−N+ $\delta_{NO_2}$(sciss) |
| 26 | $A''$ | 315s | 97m | 492 | 478 | 2.72 | 0.10 | co cn+b ch+bccl |
| 27 | $A''$ | 266s | 62m | 434 | 431 | 6.88 | 0.06 | UJ CN + Rasym |
| 28 | $A'$ | 190vs | | 331 | 339 | 0.85 | 0.26 | PO−N−O +PC−Cl |
| 29 | $A'$ | 92vs | | 313 | 318 | 2.03 | 4.81 | I′−C−C−C′ sCCl′sCN |
| 30 | $A''$ | | | 274 | 271 | 3.66 | 0.29 | R CCtrigd + UJCN |

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