



***Ab-initio* Hartee-Fock and Density functional theory calculations of 2-Chloro-6-methoxy-3-nitropyridine**

Bandana Sharma*, Munish K Yadav and Manoj K Singh

**Ajay Kumar Garg Engineering College, Ghaziabad
Molecular Spectroscopy and Biophysics Lab, D.N. (P.G.) College, Meerut (U.P.)*

ABSTRACT

In the present work, theoretical vibrational spectra of 2-chloro-6-methoxy-3-nitro pyridine (2, 6, 3-CMNP) were studied. The structural parameters and spectroscopic data of the molecule in the ground state were calculated by using ab-initio Hartree-Fock and Density Functional method (B3LYP) with 6-31+G(d, p) as the basis set. Scaled frequencies along with the IR, Raman intensities are presented here. Theoretical thermodynamic parameters are also tabulated. Vibrational assignments have been done by using Chemcraft and the 3D GAUSSVIEW visualization program.

Keywords: *Ab-initio*, Hartee-Fock, Density Functional Theory, 2-Chloro-6-methoxy-3-nitropyridine, Vibrational analysis.

INTRODUCTION

Pyridine and its derivatives are currently finding increasing applications for several reasons. At the outset, they represent a group of compounds used as reagent in the analytical chemistry. In addition to this 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 play a central role in the structure and the properties of nucleic acids[1]. Pyridine ring system occurs in the structures of a wide variety of natural products, pharmaceuticals and agrochemical compounds. Its biological importance is substantiated by the fact that pyridine ring plays a very important role in the fundamental metabolism [2]. Some of the amino pyridine show anesthetic properties and used as drugs for certain brain disease. In spite of these physiological applications and the consequent interest in their qualitative and quantitative characterization in aqueous solution, the quantum mechanical calculations of these compounds have not been thoroughly investigated. In recent years, *ab-initio* and density functional theory (DFT) has become a powerful tool in the investigation of molecular structure and vibrational spectra [3].

Intensive studies on pyridine and substituted pyridines have been made in the past keeping in view their industrial importance both as a fundamental building block and as solvent and reagent in organic synthesis. The purpose of present study is to perform calculations for 2-Chloro-6-

methoxy-3-nitropyridine at the HF and B3LYP level of theories using 6-31+G (d, p) basis set. Knowledge of both the molecular structure and infrared spectra of this molecule is very important for the investigation of inter- and intra-molecular interactions using vibrational spectroscopic method. Sanyal et al.[11] attempted to interpret the infrared spectra of 3-amino-2-chloropyridine without giving complete assignments. Recently, a spectroscopic study of a substituted pyridine (2-hydroxy-5-methyl-3-nitropyridine) has been made and its various vibrational modes have been assigned using a simplified picture of the molecule with methyl and nitro groups as unit entities [3]. Due to the existence of many contaminated vibrations, it would be difficult to assign the observed frequencies to a particular mode. The *ab-initio* Hartee-Fock and DFT method has become a powerful tool for the investigation of molecular structure and vibrational spectra. Literature survey reveals that no computational studies have been done so far on the title compound. The present work has been performed with a view point of getting the vibrational frequencies on an optimized geometry of the titled compound.

MATERIALS AND METHODS

Geometry optimization and vibrational frequencies of 2-chloro-6-methoxy-3-nitropyridine were calculated at the Hartee-Fock and DFT levels with B3LYP. All calculations were performed at HF and B3LYP levels on a Pentium IV personal computer using Gaussian 03W program package, invoking gradient geometry optimization. Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at Hartee-Fock level, adopting the standard 6-31G + (d, p) basis set[1]. This geometry was then re-optimized again at B3LYP level, using basis set 6-31+G (d, p). The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima. The optimized structural parameters were used in the vibrational frequency calculations at HF and DFT levels to characterize all the stationary points as minima. Then, vibrationally averaged nuclear positions of 2, 6, 3-CMNP were used for harmonic vibrational frequency calculations resulting in IR & Raman frequencies together with intensities [4]. We have utilized the gradient corrected density functional theory (DFT) [7,8,9]with three parameter hybrid functional (B3) for the exchange part and Lee-Yang-Parr(LYP) correlation function, accepted as a cost free approach for the computation of molecular structure, vibrational frequencies and energies of optimized structure.

By combining the results of GAUSSVIEW program with the symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. The defined coordinate, form a complete set and matches quite well with the motions observed using the GAUSSVIEW program.

RESULTS AND DISCUSSION

3.1 Molecular Geometry: The optimized structure parameters of 2-chloro-6-methoxy-3-nitropyridine calculated by *ab-initio* HF and DFT-B3LYP levels with 6-31+G (d, p) basis set are listed in the table 1 in accordance with the atom numbering scheme given in the figure (1). Result shows that both levels predict consistent data.

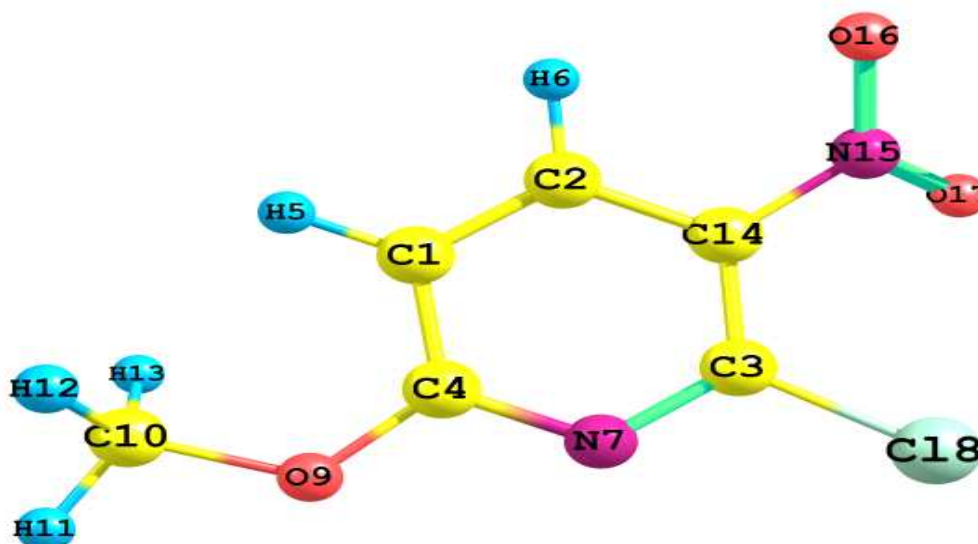


Figure 1: Optimized geometry of 2-chloro-6-methoxy-3-nitropyridine

Table 1- Optimized geometrical parameters of 2-chloro-6-methoxy-3-nitropyridine

Geometrical Parameters					
Bond	Bond Length (Å)		Bond	Bond Angle (°)	
C1-C2	1.374	1.385	C2-C1-C4	117.1	117.3
C1-C4	1.397	1.408	C2-C1-H5	120.5	120.4
C1-H5	1.07	1.084	C1-C2-H6	120.8	121.2
C2-H6	1.072	1.082	C1-C2-C14	120.2	120.2
C2-C14	1.387	1.397	C4-C1-H5	122.4	122.3
C3-N7	1.304	1.318	C1-C4-N7	122.5	122.6
C3-C18	1.722	1.742	C1-C4-O9	124	124.3
C3-C14	1.395	1.41	H6-C2-C14	119	118.6
C4-N7	1.319	1.335	C2-C14-C3	117.9	117.9
C4-O9	1.319	1.343	C2-C14-N15	117.2	117.2
O9-C10	1.409	1.43	N7-C3-C18	114.7	115.1
C10-H11	1.078	1.089	N7-C3-C14	121.9	122
C10-H12	1.084	1.096	C3-N7-C4	120.5	120.1
C10-H13	1.084	1.096	C18-C3-C14	123.4	122.9
C14-N15	1.452	1.465	C3-C14-N15	125	124.9
N15-O16	1.199	1.236	N7-C4-O9	113.6	113.2
N15-O17	1.189	1.228	C4-O9-C10	120.9	119.1
			O9-C10-H11	105.6	105.4
			O9-C10-H12	111	111
			O9-C10-H13	111	111
			H11-C10-H12	109.5	109.5
			H11-C10-H13	109.5	109.6
			H12-C10-H13	110.1	110.1
			C14-N15-O16	116.4	116.6
			C14-N15-O17	118.7	118.6
			O16-N15-O17	124.9	124.8

3.2 Vibrational assignments

According to the theoretical calculations, 2-chloro-6-methoxy-3-nitropyridine has a planar structure of the C_s point group symmetry. The three Cartesian displacements of the 17 atoms provide 45 internal modes. $\Gamma_{vib} = 31A' + 14A''$ Normal modes of vibrations. All 45 fundamental vibrations are active in both IR and Raman. For an N-atomic molecule, $2N-3$ of all vibration is in plane and $N-3$ is out of plane. Thus, for 2-chloro-6-methoxy-3-nitropyridine; 31 of all the 45 vibrations are in-plane and 14 are out-of-plane. Thus, all the vibrations of the A' species will be in plane and those of the A'' species will be out-of-plane [1]. The Harmonic vibrational frequencies calculated for 2-chloro-6-methoxy-3-nitropyridine at HF and B3LYP levels using the triple split valance basis sets along with diffuse and polarization functions, 6-31+G (d, p) have been presented in Table 2 & Table 3. The observed IR and Raman frequencies for various modes of vibrations are also presented. It is customary to scale down the calculated harmonic frequencies calculated at B3LYP level by 0.96, and those calculated at HF level were scaled by 0.89. The relative values of IR intensities and Raman scattering activities corresponding to various vibrational frequencies were calculated from the absolute values are also listed in the Table 2 & 3. The assignment of the frequencies is done by visualizing the vibrations in 3D using Gaussview and Chemcraft program. The theoretical spectrograms for IR and Raman spectra of the title molecule have been constructed and presented in Figure 2-4. Several calculated thermodynamic parameters are presented in Table 4.

3.2.1 C-H vibrations

There are two hydrogen atoms that are attached to the ring carbons. The C-H stretching modes usually appear with the strong Raman intensity and are highly polarized [4]. The C-H stretching vibrations of benzene derivatives generally appear above 3000 cm^{-1} . The C-H stretching vibrations give rise to multiple band [1] in the region $3100\text{-}3000\text{ cm}^{-1}$. The theoretical calculations shows that two scaled C-H stretching vibrations are observed at $3103, 3117\text{ cm}^{-1}$ at the HF level using 6-31+G(d, p) and the same stretching bands are observed at $3033, 3048\text{ cm}^{-1}$ at the B3LYP level using 6-31+G(d, p). So these theoretical C-H stretching vibrations are in good agreement with each other and lies well within the expected range. The in-plane bending vibrations appear in the range $1300\text{-}1000\text{ cm}^{-1}$ for the substituted benzenes and the out of plane bending vibrations occur in the frequency range $1000\text{-}750\text{ cm}^{-1}$ even though found to be contaminated [4] by C-N and C-NO₂ stretching are in the range found in the literature. C-H in plane bending vibrations are observed at $1152, 1270\text{ cm}^{-1}$ and $1150, 1190\text{ cm}^{-1}$ at the HF and B3LYP level using 6-31+G (d, p) respectively. By HF method the bands at $801, 949\text{ cm}^{-1}$ and $778, 826\text{ cm}^{-1}$ at the B3LYP level using 6-31+G (d, p) are assigned to the C-H out of plane bending vibration.

3.2.2 C-Cl Vibrations

The vibrations belonging to the bond between the ring and halogen atom [2] are worth to discuss here, since mixing of vibrations are possible due to the lowering of molecular symmetry and the presence of heavy atoms on the periphery of the molecule. In the earlier vibrational studies of 3-chloro-2-methylpyridine, 2-chloro-6-methylpyridine, 4-chloro-2-methylaniline, 5-chloro-2-methylaniline the C-Cl stretching bands are observed in the range $650\text{-}670\text{ cm}^{-1}$. Mooney [12] assigned the vibrations of C-X group (X=Cl, Br, I) in the frequency range $1129\text{-}480\text{ cm}^{-1}$. C-Cl stretching vibrations are observed at 1069 cm^{-1} and 1041 cm^{-1} in the HF and B3LYP level using 6-31+G (d, p) respectively. In the experimental spectra this stretching band is observed in the Raman spectra at 1091 cm^{-1} . $196, 197\text{ cm}^{-1}$ these two are assigned as C-Cl out of plane bending vibrations at the HF and B3LYP level using 6-31+G (d, p) respectively. The Raman band at 185 cm^{-1} is assigned to C-Cl out of plane bending. Similarly $394, 388\text{ cm}^{-1}$ are assigned to the C-Cl

in plane bending vibrations at the HF and B3LYP level using 6-31+G (d, p) respectively. In the experimental spectra of the present compound the Raman band is observed at 326 cm^{-1} . These experimental and theoretical results are in good agreement.

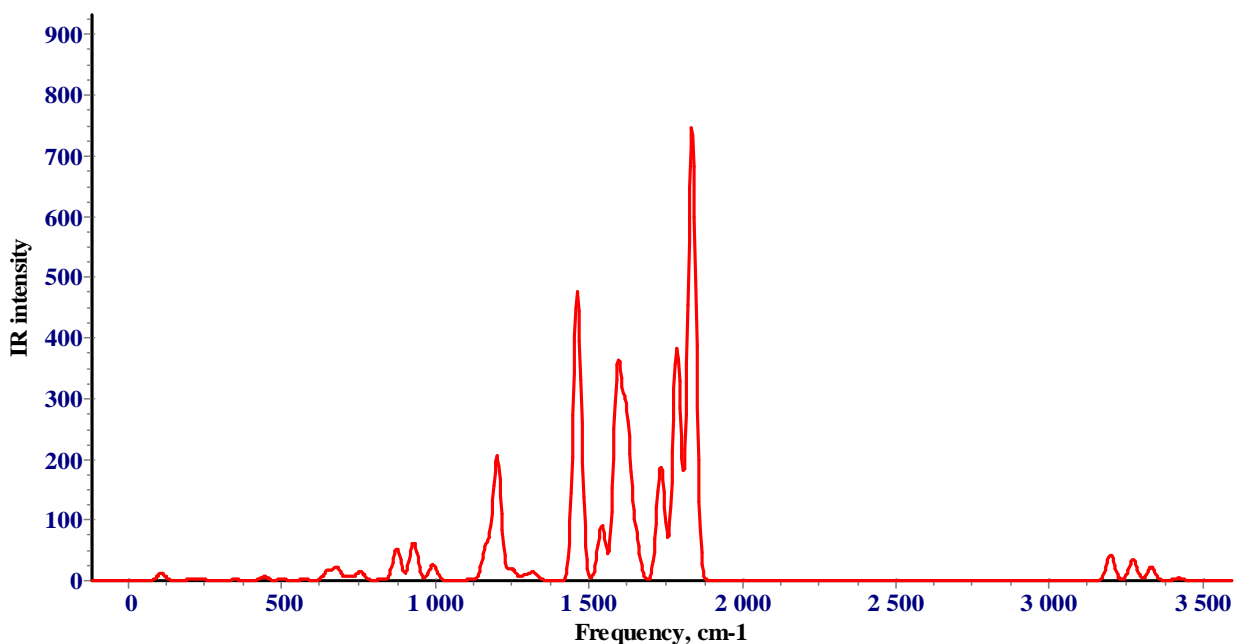


Figure 2: Theoretical IR Spectrum of 2, 6, 3-CMNP by HF/6-31+G (d, p) method.

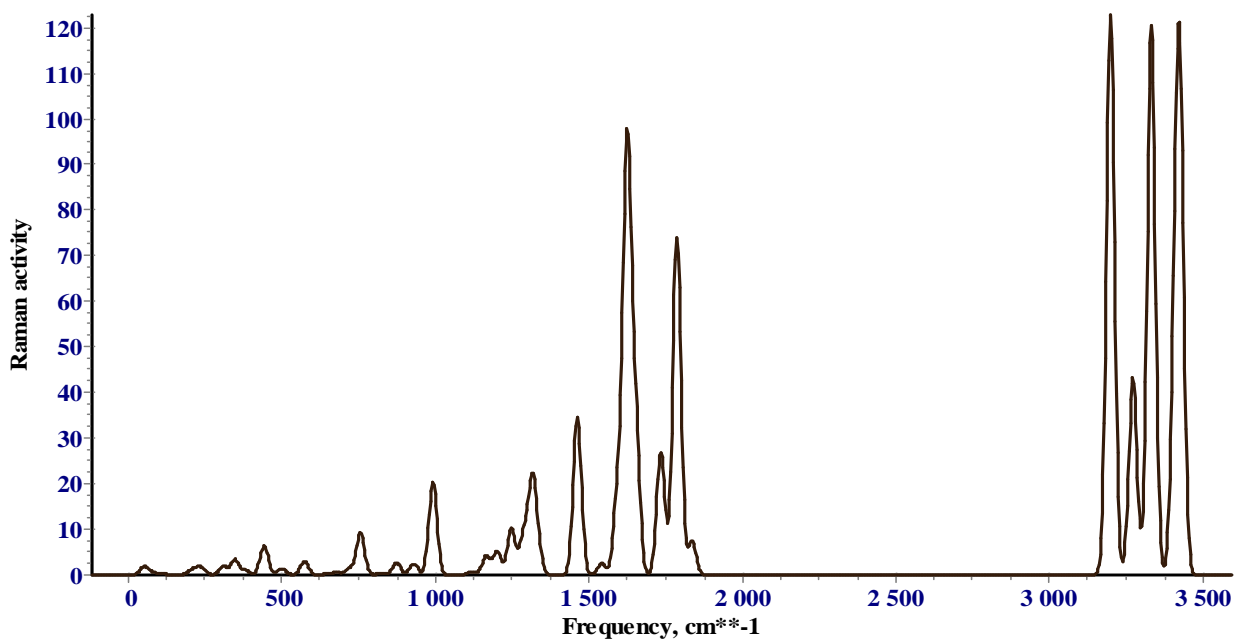


Figure 3: Theoretical Raman Spectrum of 2, 6, 3-CMNP by HF/6-31+G (d, p) method.

3.2.3 C-N Vibrations

The identification of C-N vibrations in the heterocyclic ring is found to be a difficult task since the mixing of several vibrations is possible in this region. Silverstein[13] assigned C-N stretching vibrations in the region $1382\text{--}1266\text{ cm}^{-1}$ for aromatic amines. In benzamide, the bands observed at 1368 cm^{-1} is assigned to be due to C-N stretching. In benzonitrile, the C-N stretching bands are found to be present at 1382 cm^{-1} and 1307 cm^{-1} . In the experimental spectra, this stretching vibration is observed at 1400 cm^{-1} (Raman spectra). Using Gauss view visualization program we

find that for the title compound, the C-N ring stretching corresponds to the frequency of 1373 cm^{-1} in case of HF/6-31+G(d, p) and the wave number for the same band calculated by B3LYP/6-31+G(d, p) at 1359 cm^{-1} .

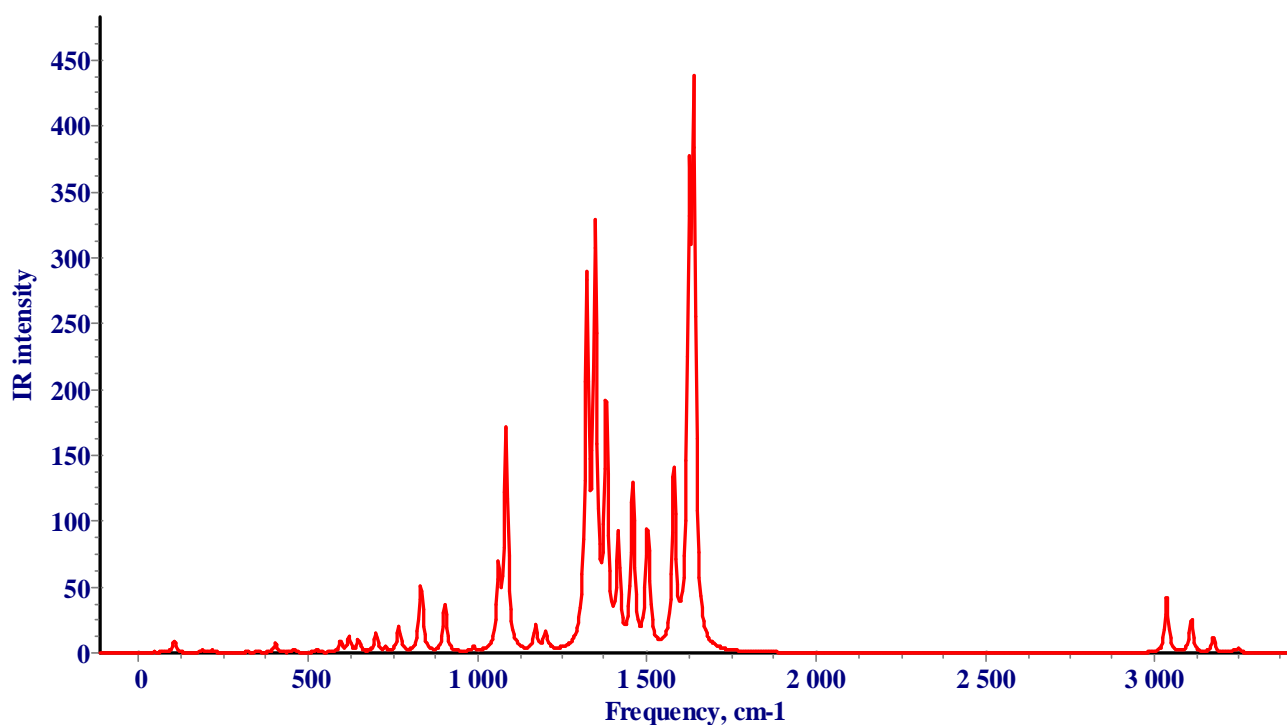


Figure 4: Theoretical IR Spectrum of 2, 6, 3-CMNP by B3LYP/6-31+G (d, p)

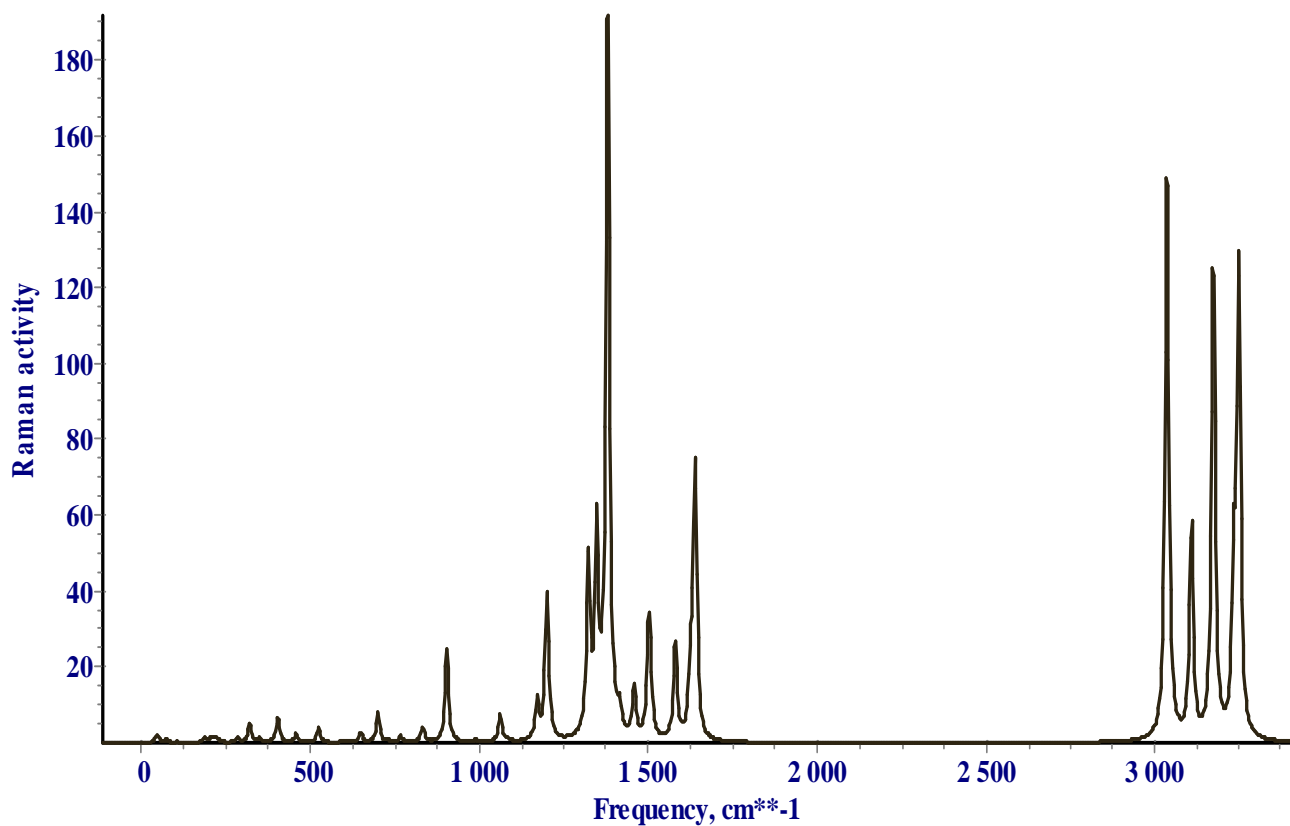


Figure 5: Theoretical Raman Spectrum of 2, 6, 3-CMNP by B3LYP/6-31+G (d, p) method.

TABLE 2: HF level computed Vibrational frequencies (cm^{-1}) obtained for 2-chloro-6-methoxy-3-nitropyridine.

S.No.	Wave number	Wave number	IR Intensity	Raman Activity	Assignments
	Unscaled	Scaled			
1	51	45	0	2	t(NO ₂)
2	77	69	0	0	ω (O-CH ₃)
3	108	96	12	0	γ (CH ₃)
4	204	181	2	1	t(CH ₃), γ (NO ₂)
5	221	196	0	1	γ (C-Cl)
6	233	208	2	1	tCH ₃
7	243	216	1	1	γ (C-NO ₂)
8	310	276	0	2	γ (C-NO ₂)
9	348	309	2	3	(C-O-C) bending
10	382	340	0	1	β (C-C-C)
11	443	394	6	6	β (C-Cl)
12	500	445	3	1	γ (C-C-C), β (C-H)
13	574	511	2	3	γ (C-C-C), γ (C-O-C)
14	649	578	15	0	ρ (NO ₂)
15	679	605	21	1	β (C-C-C), β (C-N-C)
16	720	641	7	1	γ (C-H)
17	756	673	15	9	β (C-C-C), ν (C-Cl)
18	821	731	2	0	γ (C-H)
19	874	778	52	3	γ (C-H), ω (NO ₂)
20	928	826	33	1	β (C-H)
21	931	829	30	1	δ (NO ₂)
22	992	883	26	20	γ (C-H)
23	1118	995	2	1	γ (C-H)
24	1165	1037	56	4	Trigonal bending
25	1201	1069	204	5	ν (C-Cl), ν (C-O)
26	1248	1110	20	10	γ (C-H), β (C-C-C)
27	1282	1141	3	2	ρ (CH ₃)
28	1292	1150	5	8	β (C-H)
29	1318	1173	12	20	β (C-H), ρ (CH ₃)
30	1337	1190	2	3	β (C-H)
31	1463	1302	478	35	ν (C-O), β_{sym} (CH ₃)
32	1542	1373	90	3	ν (C-N), γ (C-H), ν (C-C)
33	1594	1419	337	17	ρ (CH ₃)
34	1623	1444	242	76	CH ₃ sym. Bend, ν_s NO ₂ , ν (C-NO ₂)
35	1632	1452	9	16	CH ₃ sym. Bending
36	1633	1453	6	6	CH ₃ asym. Bending
37	1653	1471	69	31	CH ₃ asym. Bending
38	1734	1544	188	27	ν (C-C)
39	1787	1590	384	74	ν (C-C-C), ν (CNC)
40	1836	1634	747	7	ν_{asy} NO ₂
41	3199	2847	43	123	ν_{sy} CH ₃
42	3272	2912	36	43	ν_{asy} CH ₃
43	3332	2965	22	121	ν_{asy} CH ₃
44	3408	3033	1	39	ν (C-H)
45	3425	3048	4	102	ν (C-H)

TABLE 3: B3LYP level computed vibrational frequencies (cm⁻¹) obtained for 2-chloro-6-methoxy-3-nitropyridine

S. No.	Wavenumber	Wavenumber	IR Intensity	Raman Intensity	Assignments
	Unscaled	Scaled			
1	46	44	0	2	t(NO ₂)
2	73	70	1	1	ω(O-CH ₃)
3	105	101	9	0	γ(CH ₃)
4	188	180	2	1	C-O bending
5	205	197	1	1	t(CH ₃), γ(C-Cl)
6	215	206	1	1	β(CH ₃), β(NO ₂)
7	225	216	1	1	t(CH ₃)
8	285	274	0	1	t(CH ₃), ring torsional
9	321	308	1	5	C-O-C bending
10	350	336	1	1	C-O-C bending
11	404	388	7	7	β(C-Cl)
12	458	440	3	2	β(C-H)
13	524	504	2	4	γ(C-O-C)
14	596	572	8	0	ρ(NO ₂), γ(C-O-C)
15	621	596	11	0	γ(NO ₂), C-N-C bending
16	649	623	9	3	β(C-H), β(C-C-C)
17	700	672	15	8	ν(C-Cl), β(C-C-C)
18	728	699	3	0	γ(C-H)
19	768	737	20	2	ω(NO ₂)
20	832	798	22	3	δ(NO ₂)
21	834	801	32	1	β(C-H)
22	904	868	36	25	ring breathing
23	989	949	3	1	γ(C-H)
24	1062	1020	57	7	β(C-N-C), β(C-C-C)
25	1085	1041	176	1	ν(O-C), ν(C-Cl)
26	1171	1124	12	7	ρCH ₃ , γ(C-H)
27	1171	1124	7	4	ρCH ₃ , γ(C-H)
28	1200	1152	11	34	β(C-H)
29	1204	1156	5	8	ρCH ₃
30	1323	1270	281	48	β(C-H), ν(C-O)
31	1348	1294	313	54	ν(C-C)
32	1380	1325	183	200	ν(C-N), ν _s NO ₂
33	1415	1359	84	6	ν(C-N), γ(C-H)
34	1458	1400	124	13	CH ₃ sym. Bending
35	1500	1440	59	13	CH ₃ sym. Bending
36	1503	1443	11	17	CH ₃ asym. Bending
37	1506	1446	34	7	CH ₃ asym. Bending
38	1580	1517	134	26	ν(C-C), β(C-N-C)
39	1625	1560	309	17	ν(C-C), ν _{as} NO ₂
40	1639	1573	386	73	ν(C-N-C), ν(C-C)
41	3035	2914	44	156	ν _{sym} CH ₃
42	3107	2983	26	57	ν _{asym} CH ₃
43	3172	3045	11	129	ν _{asym} CH ₃
44	3233	3103	2	42	ν(C-H)
45	3247	3117	3	126	ν(C-H)

Where ν -stretching, ν_s -symmetric stretching, ν_{as} -asymmetric stretching, β -in plane bending, γ -out of plane bending, ω -wagging, t -torsion, ρ -rocking, δ -scissoring

The theoretically computed values of C=N and C-N stretching vibrations also falls in the region 1441-1242 cm^{-1} . These vibrations are almost mixed up with the C-C stretching and C-H in plane bending vibrations.

3.2.4 C-C Vibrations

C-C stretching of the ring carbon atoms is prominent. This is reflected by their high relative intensities as presented in the Table2 & 3. In general, the bands around 1400-1650 cm^{-1} in benzene derivatives are assigned to skeletal stretching C-C bands [4]. The C-C stretching vibrations at the HF/6-31+G (d, p) are observed at 1294, 1517, 1560, 1570 cm^{-1} . 1373, 1544 and 1590 cm^{-1} these wave numbers are assigned to the C-C stretching vibrations at the B3LYP/6-31+G (d, p) set. Theoretical results of HF and DFT are in good agreement with each other. Theoretically calculated C-C-C out of plane and C-C-C in plane bending modes are shown in the Table 2 & 3.

Table 4: Theoretically computed Energies (a. u.), Zero point Vibrational Energies (kcal/ mol), Rotational Constants (GHz), Entropies (cal/mol-Kelvin, Thermal Energy (kcal/mol) and Specific Heat (cal/mol-Kelvin) for 2-Chloro-6-Methoxy-3-Nitro Pyridine.

Parameters	HF/6-31+G(d, p)	B3LYP/6-31+G(d, p)
Total Energy	-1022.96	-1026.93
Zero Point Vibrational Energy	77.39590	71.45677
Rotational constants	1.48270	1.44979
	0.56381	0.55146
	0.41541	0.40644
Energy (Thermal Energy)		
Total	83.601	78.055
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	81.823	76.278
Specific Heat		
Total	35.212	37.823
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	29.250	31.861
Entropy		
Total	100.359	102.954
Translational	41.600	41.600
Rotational	31.204	31.270
Vibrational	27.554	30.084

3.2.5 Internal vibrations of the NO₂ group

The most characteristic bands in the spectra of nitro groups are due to NO₂ stretching vibrations, which are the two most useful group wave numbers, not only because of their spectral position but also for their strong intensity [1]. In nitro compounds the anti symmetric NO₂ stretching vibrations are located in the region 1580±80 cm^{-1} . The symmetric NO₂ stretching vibrations are expected in the region 1380±20 cm^{-1} . Earlier researchers [2,3] have found that for 3-bromo-2-nitropyridine the NO₂ anti symmetric & symmetric stretching vibrations at 1529 and 1350 cm^{-1} respectively. The NO₂ anti symmetric & symmetric stretching vibrations are observed at 1560, 1325 cm^{-1} at the B3LYP/6-31+G (d, p) level respectively. At the HF/6-31+G (d, p) level these two stretching vibrations are observed at 1634, 1444 cm^{-1} . The deformations vibrations of NO₂ group (Scissoring, wagging, rocking and twisting) contribute to several normal modes in the low frequency region [10]. The NO₂ scissor occurs in the region 805±60 cm^{-1} when conjugated to C=C or aromatic molecules, according to some investigators, with a contribution of the ν (CN)

which is expected to be near 1120 cm^{-1} . For the title compound, DFT calculations show the band at 798 cm^{-1} . The wave number calculated by HF/6-31+G (d, p) method for this mode is 829 cm^{-1} . In aromatic compounds, the wagging mode ω NO₂ is assigned at $740\pm 50\text{ cm}^{-1}$ with a moderate to strong intensity, a region in which γ CH is also active. For the present compound, the ω NO₂ is reported at 737 cm^{-1} by B3LYP/6-31+G (d, p) method and at 778 cm^{-1} by the HF/6-31+G (d, p) method. In rocking mode the rocking mode ρ NO₂ is active [2] in the region $545\pm 45\text{ cm}^{-1}$. Nitrobenzene shows this rocking mode at 531 cm^{-1} . According to the DFT calculations this rocking mode is obtained at 572 cm^{-1} . By using the HF/6-31+G (d, p) the rocking mode is observed at 578 cm^{-1} . NO₂ torsion mode by HF/6-31+G (d, p) method is identified at 44 cm^{-1} and by using B3LYP method at 45 cm^{-1} .

3.2.6 Methoxy group vibrations

The compound 2, 6, 3-CMNP has only one methoxy group at the 6th position; therefore there will be only one O-CH₃ stretching mode. In case of HF/6-31+G (d, p) this O-C stretching vibration is observed at 1041 cm^{-1} and by the DFT calculations observed at 1069 cm^{-1} . Each CH₃ or OCH₃ group rise to three C-H valance oscillations ($2800\text{-}3000\text{ cm}^{-1}$) and three C-H deformations as suggested by Bellamy [14]. By applying the HF/6-31+G (d, p) method the C-H asymmetric stretching bands are observed at $2912, 2965\text{ cm}^{-1}$ and C-H symmetric stretching is observed at 2847 cm^{-1} . By using the DFT calculations the C-H asymmetric stretching bands are observed at $2983, 3045\text{ cm}^{-1}$ and C-H symmetric stretching is observed at 2914 cm^{-1} . Since this molecule consist of one methoxy group, so due to the methoxy group, two CH₃ rocking modes are expected in the present molecule. CH₃ rocking mode is identified at 1141 cm^{-1} by HF method and at 1124 cm^{-1} by DFT calculations. CH₃ torsional mode is identified at 208 cm^{-1} by HF method and 216 cm^{-1} by using DFT calculations. OCH₃ torsional mode is calculated by HF at 69 cm^{-1} and at 70 cm^{-1} by using DFT.

CONCLUSION

Attempts have been made in the present work for the proper frequency assignments for the compound 2-Chloro-6-methoxy-3-nitropyridine from the theoretical IR and Raman spectra. The equilibrium geometries and harmonic frequencies of 2,6,3-CMNP were determined and analyzed both at HF and DFT level of theories using 6-31+G(d, p) basis set, giving allowance for the lone pairs through diffuse functions. The difference between the observed and scaled wave number values of most of the fundamental is very small.

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