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Quantum chemical computations on structural elucidation, homo-lumo and NLO analysis of 5-chloro-2-hydroxypyridine

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Abstract: *The FT-IR and FT-Raman spectra of 5-chloro-2-hydroxypyridinein have been recorded and analyzed. Density functional method (HF and B3LYP level with the 6-311++G(d, p) basis sets) has been used to compute optimized geometry, vibrational wave numbers of the 5-chloro-2-hydroxypyridinein. The HOMO, LUMO energy and the energy gap between them also calculated. The HOMO-LUMO energy gap explains the charge transfer interaction within the molecule. The first order hyperpolarizability also theoretically predicted to confirm the NLO activity of the molecule.*

I. INTRODUCTION

The pyridine derivatives have an important position among the heterocyclic compounds because they can be used as nonlinear materials and photo chemicals [1-3]. The study of the vibrational spectra of substituted pyridine attracts the attention of many spectroscopists due to their wide application in pharmacology and agro-chemistry. Pyridine heterocyclic are a repeated moiety in many large molecules with interesting photo physical, electrochemical and catalytic applications [3]. They serve as good anesthetic agents and used in the preparation of drugs for certain brain diseases. These pharmaceutically acceptable salts and the pre-drugs are used for the treatment (or) prevention of diabetic neuropathy [4-5]. The pharmaceutical development of nitro pyridine derivatives has received considerable attention, since they have been fully employed as chiral nucleophilic catalysts in a wide range of asymmetric synthetic process. The vibrational spectra of substituted pyridine have been the subject of several investigations [6-8]. More recently [9], FT-IR and FT-Raman spectra of nitro pyridine have been reported together with the vibrational assignments of the normal modes. However, the detailed HF/B3LYP at 6-311++G(d, p) comparative studies on the complete FT-IR and FT-Raman spectra of 5-chloro-2-hydroxypyridine (CHP) 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 ab initio (HF), and B3LYP at 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. In DFT methods, Becke's three parameter exact exchange-functional (B3) [10] combined with gradient-corrected correlational functional of Lee, Yang and Parr (LYP) [11-12] are the best in predicting the results for molecular geometry and vibrational wave numbers for moderately larger molecule. The optimized geometrical parameters, fundamental vibrational frequencies, IR intensity, Raman activity, atomic charges, dipole moment, force constants, depolarization ratio and other thermodynamic parameters and energy gap through HOMO and LUMO energy were calculated using the Gaussian 09W packages.

II. EXPERIMENTAL DETAILS

The compound under investigation namely 5-chloro-2-hydroxypyridine (CHP) was purchased from Lancaster Chemical Company (U.K.) and used as such for recording the spectra without any further purification. The FT-IR spectrum of CHP was measured in the region 4000-400 cm^{-1} has been recorded with a BRUKER IFS 66V spectrophotometer using KBr pellet. The FT-Raman spectrum of the title compound was recorded in the region 3500-50 cm^{-1} with a BRUKER RFS 100/s 66 V spectrophotometer using KBr pellet technique. Raman module equipped with Nd:YAG laser source operating at 1064 nm line width 150 mw power. The spectra were recorded with a scanning speed of 50 $\text{cm}^{-1} \text{min}^{-1}$ of spectral width 4 cm^{-1} . The reported wave numbers are believed to be accurate within $\pm 1 \text{cm}^{-1}$.



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III. COMPUTATIONAL DETAILS

Quantum chemical density functional theory calculations were carried out using the 2009 version of the Gaussian program package [13] with HF and B3LYP functions combined with the standard 6-311++G(d,p) basis sets. The Cartesian representation of the theoretical force constants has been computed at the optimized geometry by assuming C_1 point group symmetry.

Scaling of the force field was performed according to the SQM procedure using selective scaling in the natural internal coordinate representation. Transformation of the force field and the subsequent normal coordinate analysis (NCA) including the least squares refinement of the scaling factors, and calculation of total energy distribution (TED) were done on a PC with the MOLVIB program (version 7.0-G77) written by Sundies [14-16].

From the intensity theory of Raman scattering [17-19], the relative Raman intensities (I_i) and Raman activities (S_i) were calculated using the Gaussian 09W Program.

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i \left(1 - \exp\left(-\frac{hcv_i}{kT}\right) \right)} \quad \dots (4.1)$$

where v_0 is the exciting frequency (in cm^{-1}), v_i is the vibrational wave number of the i^{th} normal mode, h , c and k are fundamental constants, and f is the normalization factor for all peak intensities.

IV. RESULTS AND DISCUSSION

A. Geometry Optimization

The molecular structure with the numbering scheme is shown in Fig.1.

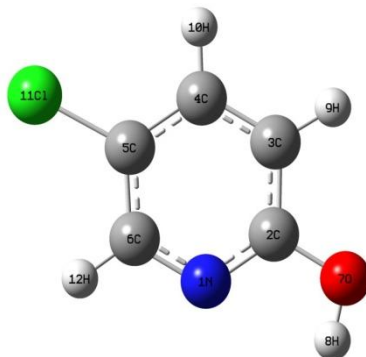


Fig.1: Molecular structure of 5-chloro-2-hydroxypyridine

Geometry optimization was performed on the compound yielding the C_1 symmetry. Table 1 presents the optimized parameters calculated at the selected two levels of theory namely HF/6-311++G (d,p) and B3LYP/6-311++G(d,p). Structural data provided in Table.1 indicates that various bond lengths are found to be almost same at B3LYP/ 6-311++G (d,p) and HF/6-311++G (d,p) levels. A detailed description of vibrational modes can be given by means of normal coordinate analysis. From the optimized geometry it shows that the DFT level calculation gives the better result than the HF level calculation.

Table 1: Optimized geometrical parameters of 5-chloro-2-hydroxypyridine obtained by B3LYP/6-311++G(d,p) and HF/6-311++(d,p) level calculations

Bond Length	Value (Å)		Bond angle	Value (°)		Dihedral Angle	Value (°)	
	B3LYP/ P/ 6- 311++ G(d,p)	HF/ 6-311++ G(d,p)		B3LYP/ 6- 311++G(d,p)	HF/ 6- 311++G(d,p)		B3LYP/ 6- 311++G(d,p)	HF/ 6- 311++G(d,p)
N1-C2	1.32	1.30	C2-N1-C6	118.39	118.55	C6-N1-C2-C3	-0.002	0.006
N1-C6	1.33	1.32	N1-C2-C3	123.68	123.68	C6-N1-C2-O7	180.006	180



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C2-C3	1.40	1.39	N1-C2-O7	117.69	118.09	C2-N1-C6-C5	0.004	0.003
C2-O7	1.35	1.33	C3-C2-O7	118.61	118.22	C2-N1-C6-H12	-179.99	-179.9
C3-C4	1.38	1.37	C2-C3-C4	117.76	117.55	N1-C2-C3-C4	-0.0007	-0.01
C3-H9	1.08	1.07	C2-C3-H9	120.27	120.15	N1-C2-C3-H9	179.99	179.98
C4-C5	1.39	1.39	C4-C3-H9	121.95	122.28	O7-C2-C3-C4	-180.01	179.98
C4-H10	1.08	1.07	C3-C4-C5	118.72	118.87	O7-C2-C3-H9	-0.01	-0.01
C5-C6	1.38	1.37	C3-C4-H10	120.89	120.83	N1-C2-O7-H8	0.04	-0.01
C5-C11	1.75	1.74	C5-C4-H10	120.38	120.29	C3-C2-O7-H8	180.04	-180
C6-H12	1.08	1.07	C4-C5-C6	119.23	118.79	C2-C3-C4-C5	0.002	0.006
O7-H8	0.96	0.94	C4-C5-C11	120.60	120.68	C2-C3-C4-H10	179.99	180
			C6-C5-C11	120.16	120.52	H9-C3-C4-C5	-179.99	-179.9
			N1-C6-C5	122.19	122.53	H9-C3-C4-H10	0.001	0.002
			N1-C6-H12	116.96	116.70	C3-C4-C5-C6	-0.0002	0.002
			C5-C6-H12	120.84	120.76	C3-C4-C5-C11	-179.99	179.99
			C2-O7-H8	107.02	108.74	H10-C4-C5-C6	-179.99	-179.9
					H10-C4-C5-C11	0.004	0.001	
					C4-C5-C6-N1	-0.003	-0.007	
					C4-C5-C6-H12	179.99	179.99	
					C11-C5-C6-N1	179.99	179.99	
					C11-C5-C6-H12	-0.002	0.0005	

B. Vibrational Spectra

The title compound consists of 12 atoms and its 30 normal modes are distributed amongst the symmetry species as

$$\Gamma_{3N-6} = 21A' \text{ (in-plane)} + 9A'' \text{ (out-of-plane)}$$

All the vibrations are active both in the Raman scattering and infrared absorption. The vibrational frequencies calculated for CHP at ab initio and DFT (B3LYP) level using 6-311++G(d,p) basis set have been collected in Table 2 along with the observed FT-IR and FT-Raman Spectral data. For visual comparison, the observed and calculated FT-IR and FT Raman spectra of CHP at HF and DFT-B3LYP level using 6-311++G(d,p) basis set are shown in Figs.2 and 3, respectively.

C-C vibrations

Benzene possesses six stretching vibrations of which the four with highest wave numbers occurring near 1650-1400 cm^{-1} are good group vibrations [20]. With heavy substituents, the bonds tend to shift to somewhat lower wave numbers and greater the numbers of substituents on the ring, broader are the absorption regions. In the title molecule, the FT-IR bands observed at 1614, 1554, 992 cm^{-1} and 1621, 1548, 1040 and 826 cm^{-1} in FT-Raman have been assigned to C-C stretching vibrations are due to the substituent's in benzene ring. The higher percentage of total energy distribution (TED) obtained for this group is encouraging and confirms the assignments proposed in this study for C-C stretching vibrations. The in-plane and out-of-plane bending vibrations of C-C group are also listed in Table 2.

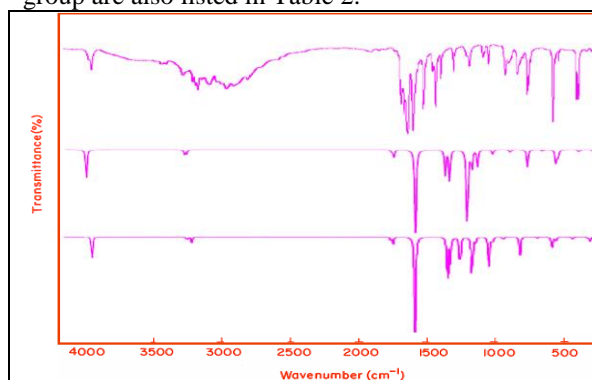


Fig. 2: Comparison of observed and calculated FTIR Spectra of 5-chloro-2-hydroxypyridine (a) Observed in solid phase (b) calculated with B3LYP/6-311++G(d,p) and (c) calculated with HF/6-311++G(d,p)

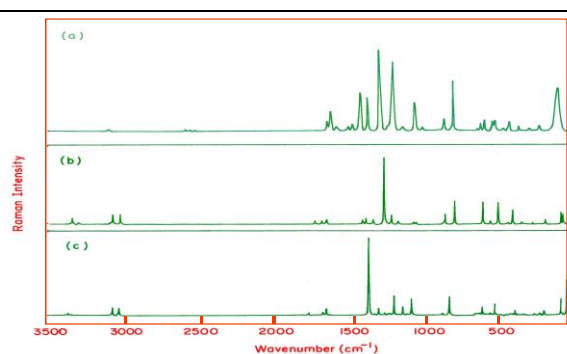


Fig. 3: Comparison of observed and calculated FT-Raman Spectra of 5-chloro-2-hydroxypyridine (a) Observed in solid phase (b) calculated with B3LYP/6-311++G(d,p) and (c) calculated with HF/6-311++G(d,p)



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Table 2: The observed FT-IR, FT-Raman vibration and their tentative Assignment

Observed frequency (cm ⁻¹)		Calculated frequency (cm ⁻¹)		TED (%) among type of internal coordinates
FT-IR	FT-Raman	B3LYP/6-311++G(d,p)	HF/6-311++G(d,p)	
3700 vw	-	3707	3692	OH(100)
3133 m	3130 m	3105	3113	CH(99)
3084 ms	3084 w	3090	3090	CH(99)
3057 s	3035 w	3074	3090	CH(99)
1614 vs	1621 vw	1618	1626	CC(56), bCH(14), CN(11), Rsymd(8)
1554 vs	1548 m	1552	1562	CC(43), CN(27), bCH(11), Rasynd(10)
1470 s	1472 ms	1467	1470	bCH(48), CC(20), CN(16), CO(12)
1426 s	1426 s	1401	1422	CN(37), CC(20), bCOH(14), bCH(11), bCCI(5), bCO(5)
1332 ms	1340 vw	1332	1335	bCH(55), bCOH(16), CC(14), CN(10)
-	1267 m	1286	1267	CO(45), CN(19), bCH(18), Rtrigd(12)
1235 m	-	1240	1231	CN(50), CC(32), bCH(14)
1153 m	1158 s	1160	1156	bCOH(39), CC(25), bCH(14), CN(14)
1118 m	1119 vw	1115	1117	bCH(59), CC(20), CN(8), bCOH(7)
992 ms	1040 vs	1095	1070	CC(46), CCl(24), bCH(18), Rtrigd(5)
973 w	990 w	995	997	Rtrigd(56), CN(17), CC(14), bCH(7), CCl(5)
920 m	930 w	946	978	gCH(90)
850 m	842 w	906	943	gCH(86), tring(7)
-	826 w	843	834	CC(28), CO(21), Rasynd(20), Rtrigd(12), CN(11)
-	813 s	817	829	gCH(72), gCO(14), tRsymd(7)
668 s	670 w	729	740	tring(61), gCO(24), gCH(8), gCCI(6)
638 w	643 w	646	646	CCl(34), Rsymd(22), Rasynd(14), CO(11), Rtrigd(9), CC(6)
616 s	620 s	629	629	Rsymd(45), Rasynd(31), CC(9), bCO(7)
503 w	508 w	526	522	gCO(25), tRsymd(23), gCCI(21), tring(14), tOH(12)
415s	-	463	439	tOH(57), tRsymd(15), gCCI(11), gCO(11)
-	416 s	427	434	bCO(60), Rsymd(13), bCCI(9), bCOH(5)
-	-	418	419	tRasynd(83), gCH(12)
-	315 ms	376	376	Rasynd(39), CCl(27), Rsymd(18), CC(7)
-	281 vw	308	314	gCCI(49), tRsymd(14), tring(13), tRasynd(9), gCH(9), gCO(6)
-	244 vw	249	252	bCCI(78), bCO(11)
-	126 ms	117	122	tRsymd(74), gCCI(12), gCH(10)

Abbreviations: *b*-bending; *g*-out-of-plane bending; *t*-torsion; *R*-ring;; *asym*-assymetic; *sym*-symmetric; *vs*-very strong; *s*-strong; *ms*-medium strong; *m*-medium; *w*-weak; *vw*-very weak.

C-H vibrations

The hetroaromatic structure shows the presence of C-H stretching vibrations in the region 3100-3000 cm⁻¹[21-23]. This is the characteristic region for the ready identification of C-H stretching vibrations. In this region, the bands are not affected appreciably by the nature of the substitutions. In the present investigation, the C-H stretching vibrations are observed at 3133, 3084 and 3057 cm⁻¹ in the FT-IR spectrum and at 3130, 3084 and 3035 cm⁻¹ in the Raman for CHP. The C-H in-plane and out-of-plane bending vibrations of the title compound have also been identified and listed in Table 3.

O-H vibrations

The precise positions of O-H band are dependent on the strength of hydrogen bond. The O-H stretching vibration is normally observed at about 3300 cm⁻¹. The O-H in-plane bending vibration is observed in the region 1440-1260 cm⁻¹ [24-25]. In CHP, the band appeared at 3700 cm⁻¹ in FT-IR spectrum were assigned to O-H stretching modes of vibrations. The in-plane bending vibrations of hydroxy groups have been identified at 1153, 1158 cm⁻¹ in FT-IR and FT Raman respectively. O-H out-of-plane vibration of the title compound have also been identified and listed in Table 3.



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C-Cl vibrations

The C–Cl stretching vibrations generally give strong bands in the region $760\text{--}505\text{ cm}^{-1}$ [25]. The FT-IR and FT-Raman bands observed at 638 cm^{-1} and 643 cm^{-1} have been assigned to C–Cl stretching vibrations respectively. Most of the aromatic chloro compounds have a band of strong-to-medium intensity in the region $385\text{--}265\text{ cm}^{-1}$ due to C–Cl in-plane bending vibrations. Accordingly, the FT-Raman band identified at 244 cm^{-1} has been assigned to the C–Cl in-plane bending mode. The C–Cl out of plane deformation vibration has been established at 281 cm^{-1} in FT-Raman spectrum.

C-O vibrations

If a compound contains a carbonyl group the absorption caused by C–O stretching is generally among the strongest present and occur in the region $1260\text{--}1000\text{ cm}^{-1}$. Hence, in the present investigation the FT-Raman band at 1267 cm^{-1} is assigned to C–O stretching vibration of CHP. The in-plane and out-of-plane vibrations of C–O group are presented in Table 3.

C–N vibrations

In aromatic compounds, the C–N stretching vibrations usually lie in the region $1400\text{--}1200\text{ cm}^{-1}$ [26]. In the present investigation, the FT-IR band appeared at 1426 and 1235 cm^{-1} and FT-Raman band appeared at 1426 cm^{-1} in CHP have been designated to C–N stretching vibrations. The in-plane and out-of-plane bending vibrations assigned in this study are also supported by the literature [27]. The identification of C–N vibration is a difficult task, since it falls in a complicated region of the vibrational spectrum. However, with the help of force field calculations, the C–N vibrations are identified and assigned in this work.

C. HOMO – LUMO BAND GAP

This electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [28]. Many organic molecule, containing conjugated π electrons are characterized by large values of molecular first hyper polarizabilities, are analyzed by means of vibrational spectroscopy. In most of the cases, even in the absence of inversion symmetry, the strongest band in the Raman spectrum is weak in the IR spectrum and vice-versa. But the intramolecular charge from the donor to acceptor group through a single-double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time. The experimental spectroscopic behavior described above is well accounted for DFT calculations in π conjugated system that predict exceptionally infrared intensities for the same normal modes. The analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state and is mainly described by one-electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied orbital (LUMO). The LUMO of π nature, (i.e. benzene ring) is delocalized over the whole C–C bond. The HOMO is located over benzene ring, iodine and the HOMO–LUMO transition implies an electron density transfer to the pyridine ring from hydroxyl group and chlorine atom. Moreover, the compositions of the frontier molecular orbital for CHP are shown in Fig. 4.

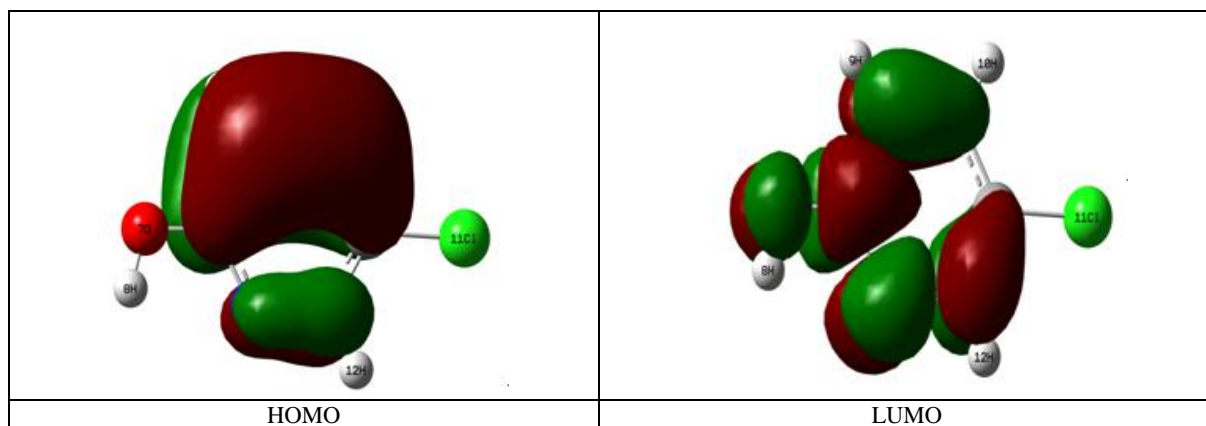


Fig. 4: HOMO-LUMO plot of 5-chloro-2-hydroxypyridine



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The HOMO-LUMO energy gap of CHP is calculated at B3LYP/6-311++G(d,p) level, which reveals that the energy gap reflects the chemical activity of the molecule. The LUMO as an electron acceptor (EA) represents the ability to obtain an electron and HOMO represents ability to donate an electron (ED). The ED groups to the efficient EA groups through π -conjugated path.

The strong charge transfer interaction through π -conjugated bridge results in substantial ground state Donor-Acceptor (DA) mixing and the appearance of a charge transfer band in the electron absorption spectrum.

HOMO energy	= -0.28463 a.u
LUMO energy	= -0.01811 a.u.
HOMO-LUMO energy gap	= -0.26652 a.u.

Table 3: HOMO-LUMO energy and other related properties of 5 chloro-2-hydroxypyridine in a.u. based on B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) methods

Parameters	B3LYP/6-311++G(d,p)	HF/6-311++G(d,p)
HOMO	-0.28463	-0.35130
LUMO	-0.01811	0.14572
Global Hardness (η)	-0.13326	-0.24851
Electronegativity (χ)	-0.15137	-0.10279
Global softness (s)	-7.50412	-4.02398
Chemical potential (μ)	0.15137	0.10279
Global Electrophilicity (ω)	-0.08597	-0.02125

The calculated self-consistent field (SCF) energy or optimized global minimum energy of CHP is -783.233 Hartrees at B3LYP/6-311++G(d,p) and -780.573 Hartrees at HF/6-311++G(d,p) methods. The calculated HOMO, LUMO and other related properties at B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) levels are listed in Table 3. The HOMO and LUMO energy gap explains the fact that eventual charge transfer interaction is taking place within the molecule.

V. PREDICTION OF FIRST HYPERPOLARIZABILITY – A NLO PROPERTY

There is an intense current research activity in the area of molecular linear and non-linear optics, devoted to the search for efficient, stable, simple organic compounds exhibiting large hyper polarizabilities. [29]. A reliable prediction of molecular hyperpolarizability requires adequate basis sets and therefore must involve both diffuse and polarization functions. As the basis becomes larger, one expects a better description of the compound and accordingly, more accurate results. In the view of these points, B3LYP/6-311++G(d,p) and B3LYP/3-21G method has been used for the present study in order to see the effect of the level of theory and basis set. The title compound was fully optimized at B3LYP/6-311++G(d,p) method in the GAUSSIAN 09W program. The tensor component of the static first hyperpolarizabilities, β , was analytically calculated by using the same method as mentioned above. From the computed tensorial component β , β_{vec} is calculated for the title compound by taking into account the Kleinman symmetry relations and the squared norm of the Cartesian expression for the β tensor [30].

The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion becomes

$$E = E^0 - \mu_a F_a - 1/2 \alpha_{\alpha\beta} F_\alpha F_\beta - 1/6 \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma + \dots$$

Where E^0 is the energy of the unperturbed molecules, F_a the field at the origin and μ_a , $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first hyperpolarizabilities, respectively. The total static dipole moment μ , the mean polarizability α_0 and the mean first hyperpolarizability β , using the x, y, z components are defined as follows,

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

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

$$\alpha = 2^{-1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2]^{1/2}$$



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$$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) / 3$$

$$\Delta\alpha = 1/2[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2]$$

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

and

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}, \beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}, \beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

The calculated first hyperpolarizability(β) for CHP is 1.9850×10^{-30} esu, and 3.2070×10^{-30} esu by B3LYP/HF with 6-311++G(d,p) methods, respectively and also Dipole moment (μ), Mean polarizability (α), Anisotropy of the polarizability ($\Delta\alpha$), Energy values are reported in Table .4. The large value of hyperpolarizability, β which is a measure of the non-linear optical activity of the molecular system, is associated with the intramolecular charge transfer, resulting from the electron cloud movement through π conjugated frame work from electron donor to electron acceptor groups. So, the title compound is an attractive object for future studies of nonlinear optical properties.

Table 4: Nonlinear optical properties of based on 5-chloro-2- hydroxypyridine based on B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) methods

NLO Behaviour	B3LYP/6-311++G(d,p)	HF/6-311++G(d,p)
Dipole moment (μ) in Debye	0.7571	0.8474
Mean polarizability (α) in esu	-52.9675 □ □ 10 □ 30	-53.1695 □ □ 10 □ 30
Total polarizability ($\Delta\alpha$)	50.7716 □ □ 10 □ 30	63.6297 □ □ 10 □ 30
First hyperpolarizability (β) in esu	1.9850 □ □ 10 □ 30	3.2070 □ □ 10 □ 30
Energy in Hartrees	-783.233	-780.573

VI. CONCLUSION

Attempts have been made in the present investigation for the molecular parameters and frequency assignments for CHP from the FT-IR and FT Raman spectra. Vibrational frequencies, infrared intensities and Raman activities are calculated and analyzed by ab initio HF and DFT (B3LYP) levels of theory utilizing 6-311++G(d,p) higher basis set. The difference between the observed and scaled wave number values of most of the fundamentals is very small. Comparison between the calculated and experimental structural parameters indicates that B3LYP results are in good agreement with experimental values. The assignments made at higher level of theory with higher basis set with only reasonable deviations from the experimental values seem to be correct. HOMO and LUMO energy gap explains the eventual charge transfer interaction taking place within the molecule. NLO properties and other molecular properties of the title compound are also studied.

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