Synthesis, Growth, Spectroscopic Studies and Computational Analysis of L- Histidine Hydrofluoride: A Nonlinear Optical Single Crystal

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ABSTRACT: *A nonlinear optical single crystal of L- Histidine Hydrofluoride (LHHF) was grown by slow evaporation method at room temperature and the grown crystal was characterized by FTIR and UV – Visible spectra. The non-centro symmetric single crystal of L- Histidine Hydrofluoride (LHHF) was crystallizes in orthorhombic crystal system with space group $P2_12_12_1$, it exhibit second order non-linear optical (NLO) susceptibility due to the intermolecular charge transfer. Density functional theory (DFT) calculations have been carried out to study the nature of hydrogen involved in the LHHF crystal. The bond lengths and bond angles of the structure of LHHF crystal calculated using B3LYP method with 6-31+G (d, p) and 6-311++ G (d, p) basis set. The linear polarizability (α) and the first order hyper polarizability (β) values of the investigated molecule have been computed. The calculated HOMO and LUMO energies indicates the charge transfer occurs within the molecule. Thermodynamic parameters such as zero point vibrational energy (ZPVE), thermal energy gap and specific heat capacity and entropy have been calculated by DFT method. Thermal analysis found that the candidate material exhibits three stages of weight loss. Low dielectric constant and dielectric loss of LHHF confirms the polarizing ability and hence NLO nature. These calculations are compared with experimental values to provide deep insight into its electronic structure and property of grown crystal.*

Keywords - *DFT, Hyperpolarizability, IR, NLO, TG/DTA, UV.*

I. INTRODUCTION

During the past few decades, the researchers are focus on new materials having the property of nonlinear optical (NLO), due to its vast applications in the field of telecommunications and optoelectronics [1]. Nowadays, amino compounds play a vital role in the field of NLO. In particular, L-Histidine has much attraction due to their unique properties and also has the ability to act as a proton donor, proton acceptor and a nucleophilic agent. These properties led to the synthesis of several new compounds of L-Histidine [2]. Based on the above, Present work deals with synthesis of L-Histidine Hydrofluoride (LHHF) single crystal and characterized by structure analysis, optical property, IR, thermal analysis, dielectric measurments, NLO as well as the theoretical study of density function theory (DFT) calculations.

II. EXPERIMENTAL PROCEDURE

L-Histidine Hydrofluoride (LHHF) was synthesised by taking L-Histidine and Hydrofluoric acid in the equimolar proportions from aqueous solutions at room temperature and the product compound L-His.HF.$2H_2O$ (LHHF) is formed. Optically good quality transparent crystals are obtained within 50 days.

III. COMPUTATIONAL DETAILS

Density functional theory calculations are performed using Gaussian'03 program package [3]. The geometries were fully optimized without any constraint. The vibration frequencies are calculated by using B3LYP/6-31+G(d, p) and B3LYP/6-311++ G(d, p) respectively. Vibration mode assignments were also compared with the experimental results.

IV. RESULTS AND DISCUSSION

4.1 Single crystal XRD analysis

Single crystal X-ray diffraction analysis of LHHF crystal was carried out and the lattice parameters are a = 8.449(2) Å, b = 8.572(3) Å, c = 13.895(4) Å and V=1006.343(3) Å^3. It has observed that LHHF belongs to orthorhombic structure with space group $P2_12_12_1$. The lattice parameters are in good agreement with the reported values [4].

4.2 Molecular Geometry

The most optimized structural parameters were calculated and the bond lengths and bond angles depend on the method and the basis set used in the calculations, and they can be used as foundation to calculate the molecular properties for the compounds. The global minimum energy was obtained by DFT methods with different basis sets (such as 6-31+G (d, p), 6-311++G (d, p)) as -797.851325 a. u and -798.12081120 a. u respectively.

4.3 Vibrational Analysis

The FT-IR spectra of LHHF, was recorded on BRUKER IFS 66V FT-IR SPECTROMETER using KBr pellet in the range 4000 cm^{-1} to 400 cm^{-1}. The title molecule LHHF has 28 atoms. It has 78 normal vibrational modes. 53 of these modes are in-plane symmetric (A′) and 25 out-of-plane symmetric (A″) with respect to the reflection on the symmetry plane.

Γ_{78} = 53 A′ (in-plane) + 25 A″(out-of-plane) respectively

Some selected vibrational assignments of fundamental modes of LHHF FT-IR experimental frequencies, calculated frequencies and vibrational assignment by DFT method is reported in Table 1. The experimental FT-IR spectrum was reported in the Fig. 1. The theoretically simulated FT-IR spectrum at B3LYP/6-31+G (d, p) and 6-311++G (d, p) basis set was shown in Fig. 2 and Fig. 3. From LHHF, the two water molecules are present, it is observed in the region of 1630.32 cm^{-1} from IR and 1631.95, 1642.86 cm^{-1} from the computed values using DFT basis sets. These stretching and bending vibrations of acid group are observed in the region 1400–1200 cm^{-1}. The presence of strong absorption bands at 1411.08, 1286.68 cm^{-1} confirms the presence of COO$^-$ groups by IR and 1430.32, 1432.77 using 6-31+ G (d, p) and 1233.32, 1225.95 cm^{-1} using 6-311++ G (d, p) basis sets. The in-plane O-H deformation vibration appears as strong band in the region 1440-1260 cm^{-1}. The strong experimentally predicted band at 1359 cm^{-1} is assigned to in-plane bending vibration of COO$^-$ group for the title molecule and it is in good agreement at 1360, 1364.13 cm^{-1} in computed FT-IR spectrum.

4.4 Hyperpolarizability studies

The calculated values of polarizability (α) and hyperpolarizability (β) of LHHF are 0.8399 x 10^{-30}esu, 0.91096 x 10^{-30}esu, 5.91506 x 10^{-30} esu and 5.80467 x 10^{-30} esu by 6-31+ G (d, p) and 6-311+ +G (d, p) basis sets respectively. It determine not only the strength of molecular interactions and the cross sections of different scattering and collision process. LHHF is an excellent NLO material which is understood from the values of polarizability and hyperpolarizability values.

4.5 HOMO-LUMO Gap

In principle, there are many ways to calculate the excitation energies. The 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). While the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. This form corresponds to the frozen orbital approximation, the ground state properties are used to calculate the excitation values. HOMO- LUMO orbital picture is shown in Fig. 4 and Fig. 5. A frontier molecular orbital analysis gives the HOMO-LUMO energy gap value as 4.178 eV and 4.260 eV for 6-31+ G (d, p) and 6-311+ +G (d, p) basis sets respectively.

4.6 UV-Vis-NIR spectrum and evaluation of linear optical constants

The optical absorption spectrum indicates that LHHF crystal has minimum absorption in the region between 240–1500 nm. As the entire visible region does not bear any absorption band it can be used for NLO applications. The values of the optical band gap E$_g$ were obtained from the intercept of (αhν)^2 versus hν curve plotted. The band gap is found to be 4.89 eV.

4.7 Thermal Analysis

The TGA and DTA thermogram of LHHF is shown in Fig.. The sharp weight loss observed at 108 °C is attributed to the loss of lattice water. This is followed by two more stages of weight loss; the first one at 241°C and the second at 327 °C, the total weight loss of these stages correspond to 63%. Hence, it is assigned to decomposition of LHHF. The resulting residue gives a weight loss for wider range of temperature between 742 °C and 1200 °C, which is found to be 37%. Since the total weight loss corresponds to 100% it clearly indicates that no residue is present after this stage. The sharp endothermic peaks in the DTA trace nearly coincide with decompositions shown in the TGA trace. Although LHHF decomposes at 241°C, the crystal structure is lost at 108 °C itself, which is assigned to the loss of lattice water. Hence, the compound can be exploited for application below 108 °C.

4.8 Dielectric studies

The dielectric nature of the grown sample is shown in Figure 3a and 3b. The lower value of dielectric constant at higher frequencies is suitable for the enhancement of SHG coefficient. The low value of dielectric loss indicates that crystal possesses the good quality. These parameters have vital importance for NLO applications.

4.9 SHG in LHHF crystal

The freshly powdered sample of particle size (around 150 μm) was illuminated using Q−switched, mode locked Nd: YAG laser with input pulse of 6.2 mJ. For a laser input pulse of 6.2 mJ, the second harmonic signal (532 nm) of 91.66 mW and 563.71 mW were obtained through KDP and LHHF samples respectively. Thus the SHG efficiency of LHHF is six times higher than KDP.
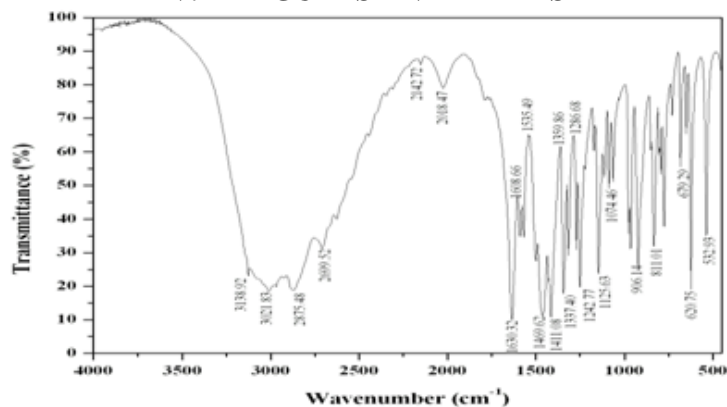
V. FIGURES AND TABLES
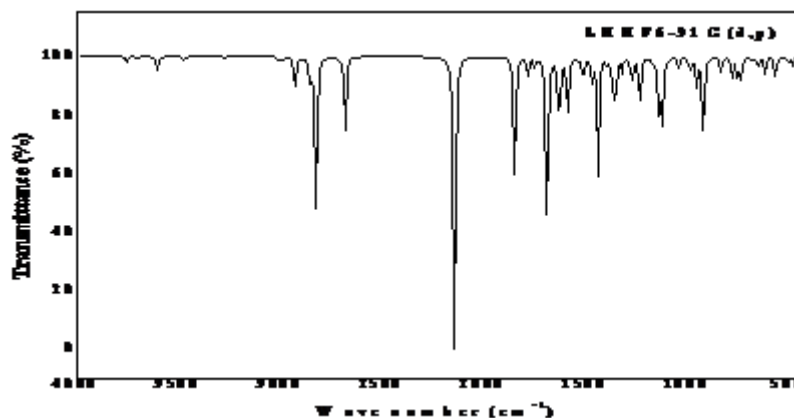

Fig 1. Experimental FT-IR Spectrum of LHHF

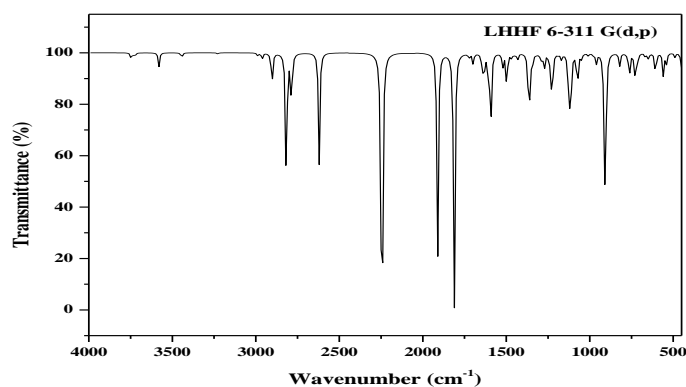**Fig 2.** Observed FT IR Spectrum of LHHF by 6-31+ G (d, p) method

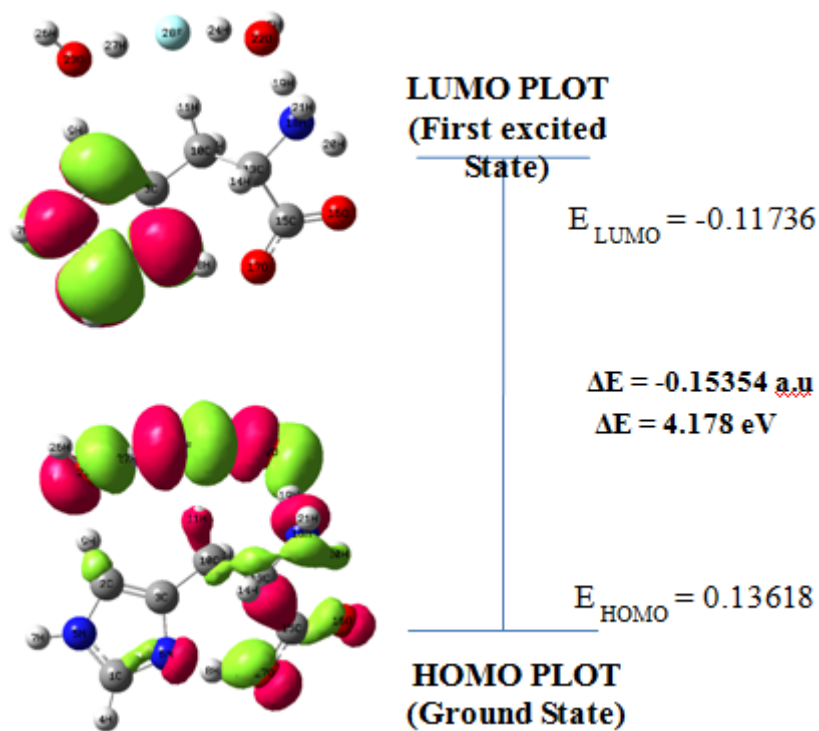Fig 3. Observed FT IR Spectrum of LHHF by 6-311++ G (d, p) method

LUMO PLOT
(First excited
State)

$E_{LUMO} = -0.11736$

$\Delta E = -0.15354$ a.u
$\Delta E = 4.178$ eV

$E_{HOMO} = 0.13618$

HOMO PLOT
(Ground State)

Fig 4. HOMO –LUMO plot of LHHF at B3LYP/6-31+G(d,p)

LUMO PLOT
(First excited
State)

$E_{LUMO} = -0.07872$

$\Delta E = -0.15657$ a.u
$\Delta E = 4.260$ eV

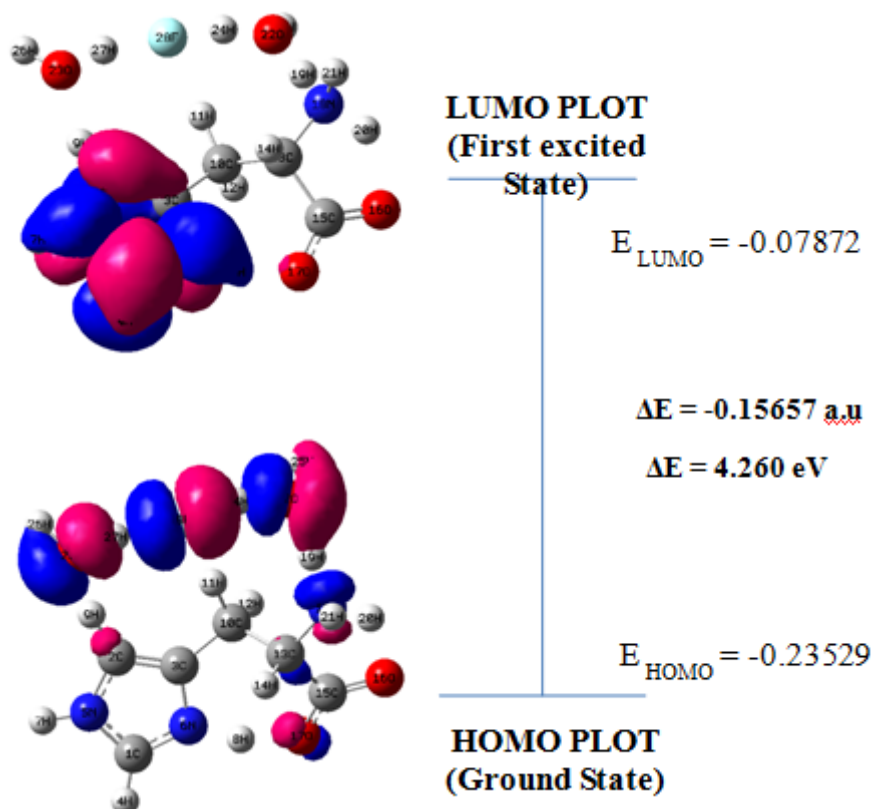$E_{HOMO} = -0.23529$

HOMO PLOT
(Ground State)

Fig 5. HOMO –LUMO plot of LHHF at B3LYP/6-311++G(d,p)

Table 1. Some selected Experimental and Calculated B3LYP/6-31+ and B3LYP/6-311++ levels of vibrational frequencies of LHHF

| Experimental Frequency (cm^{-1}) | Observed | | | | | | Assignments |
| | B3LYP/6-31+G(d,p) | | | B3LYP/6-311++G(d,p) | | | |
	FTIR frequency	Reduced mass	Force constant	FTIR frequency	Reduced mass	Force constant	
3138.92	3273.3514	1.1017	6.9552	3227.5591	1.1025	6.7665	CH$_2$ asy st
3021.83	3005.4301	1.0864	5.7818	2987.7944	1.0863	5.7135	CH st
2875.48	2845.6892	1.0641	5.0771	2817.2803	1.0693	5.0004	CH$_3$ sym st
2699.52	2681.9047	1.1242	4.7642	2620.8154	1.1410	4.6176	CH st
2142.72	2137.2235	1.0554	2.8404	2244.8411	1.0614	3.1515	CN st
1715	1748.3303	3.2182	5.7958	1723.2240	1.3890	2.4301	C OO$^-$ ast
1608.06	1622.2299	1.0431	1.6173	1607.2471	1.1274	1.7159	NH$_2$ sci
1535.49	1531.3074	3.1293	4.3233	1521.2012	2.7257	3.7163	COO$^-$ asy
1469.62	1465.5626	1.9695	2.4924	1469.8037	1.1653	1.4832	CH3 asy de
1411.08	1430.3205	1.2799	1.5428	1432.7734	1.5489	1.8734	COO$^-$ sym
1359.86	1360.4303	1.7678	1.9277	1364.1394	2.3791	2.6084	COO$^-$ ipb
1337.40	1336.8213	1.9227	2.0245	1323.5279	1.6850	1.7390	CO st
1125.63	1123.2150	1.5203	1.1301	1111.9045	1.7277	1.2585	CN st
1074.46	1093.5384	3.0164	2.1253	1073.9223	1.1082	0.7531	OH ipb
906.14	916.3631	3.4301	1.6970	900.4025	1.0997	0.5253	γ CC
811.01	827.5760	3.7957	1.5317	821.1376	4.5337	1.8011	CH opb
679.29	675.2904	3.1951	0.8584	667.1351	2.6357	0.6912	C-C b

St-stretching ; **sym st**- symmetry stretching ;**asy st**- assymtry stretching ; **sci**-scisorring **t**-twisting ;**ipb**-in-planebending ;**opb**- out-of-plane bending; **ipd**-inplane deformation **wag**- wagging; **R**-anthracene ring;; **roc**-rocking;

VI. CONCLUSION

Single crystals of LHHF are grown by slow evaporation technique in period of 50 days. XRD studies show that the grown crystal belongs to orthorhombic crystal system having non-centrosymmetry with P2$_1$2$_1$2$_1$ space group. Optimized structure of the isolated LHHF molecule obtained by DFT calculations give the minimum energy state. First order hyperpolarizability of LHHF is calculated as 5.91506× 10^{-30} esu, 5.80467 x 10^{-30} esu using 6-31+ G (d, p) and 6-311++ G (d, p) respectively. It is also found useful in molecular designing. Theoretical and experimental Spectroscopic studies exemplify the presence of various functional groups in the molecule. Both theoretically simulated and experimentally obtained FT-IR spectra show coincidence. Frontier molecular orbital analyses give the HOMO-LUMO energy gap value as 4.178 and 4.260 eV. SHG efficiency of the grown crystal shows that it is 6 times greater than KDP. From Thermal analysis it is found that the candidate material exhibits three stages of weight loss. Low dielectric constant and dielectric loss of LHHF confirms the polarizing ability and hence NLO nature.

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