

Vibrational and Homo-Lumo Analysis of L-Histidinium Dipicrate Dihydrate by Density Functional Theory

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Abstract - L-histidinium dipicrate dihydrate (LHDP), a semi organic nonlinear optical material was synthesized by slow solvent evaporation technique. Fourier transform infrared (FT-IR) spectroscopic studies were performed for identifying different functional groups present in the compound and was compared with the theoretical data obtained from DFT studies. Non-linear optical (NLO) behavior of the LHDP was investigated by the determination of hyperpolarizability β obtained by B3LYP/6-31G (d, p) method. The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) with frontier orbital gap were presented.

Keywords - LHDP, FT-IR, NLO, Hyperpolarizability, HOMO, LUMO

I. INTRODUCTION

Many investigations are being conducted to synthesize new semi organic materials with large second-order optical nonlinearities in order to satisfy day-to-day technological requirements. The basic structure of semi organic nonlinear optical (NLO) materials is based on the π bond system [1]. Due to the over-lap of π orbital, delocalization of electronic charge distribution leads to a high mobility of the electron density. Functionalization of both ends of the π bond system with appropriate electron donor and acceptor groups can increase the asymmetric electronic distribution in either or both ground and excited states, leading to an increased optical nonlinearity. Knowledge of molecular geometry may help researchers to predict the physiochemical properties of the compound material in different environment. Geometry optimization was achieved using the Gaussian 03W program package and inter atomic distances and angles were computed.

II. COMPUTATIONAL DETAILS

Quantum chemical density functional theory calculations were carried out with the 2003 version of the Gaussian program package[3] using B3LYP functions combined with the standard 6-31G (d,p) basis set. The optimized geometrical parameters, fundamental vibrational frequencies, dipole moment, hyperpolarizability and HOMO-LUMO gap were calculated.

III. RESULTS AND DISCUSSIONS

Optimized Geometry

Computational chemistry is an important tool to design and modeling the NLO materials. The geometry of the investigated compound was treated as an isolated gas molecule. Becke-Lee-Yang-Parr hybrid exchange correlation three parameter (B3LYP) level at 6-31G basis set is used to derive the optimized structure in Gaussian 03W. Optimized structure was confirmed to be minimum energy conformations. The optimized molecular structure of the isolated LHDP is shown in figure 1.

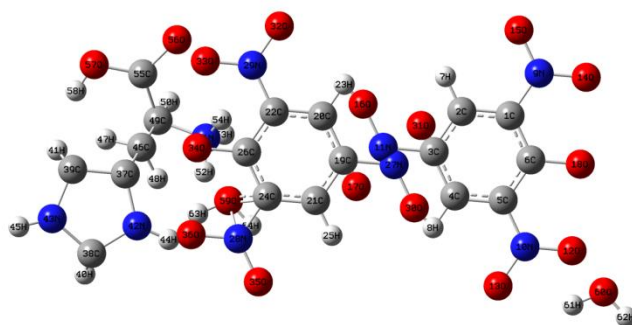


Figure 1. Molecular structure of LHDP

Vibrational analysis

The title molecule LHDP has 64 atoms. It has 186 ($3N - 6$) normal vibrational modes. The 186 normal modes of LHDP are distributed amongst the symmetry species as $\Gamma_{\text{vib}} = 125 A' \text{ (in-plane)} + 61 A'' \text{ (out-of-plane)}$. All the 186 fundamental vibrations are active in Infrared absorption. Selected vibrational assignments of LHDP for the experimental FT-IR frequencies along with the calculated frequencies are tabulated in Table 1.

First order Hyperpolarizability studies

Experimental measurements and theoretical calculations on molecular hyperpolarizability β become one of the key factors in the second-order NLO materials design [4]. It also provides a guideline to experimentalists for the design and synthesis of semi organic NLO materials. The non linear response, linear polarisability (α_{ij}) and first order hyperpolarisability (β_{ijk}) can be related as a Taylor expansion of the total dipole moment as

$$\mu_t = \mu_0 + \alpha_{ij}E_i + \beta_{ijk}E_iE_j + \dots \quad (1)$$

Table 1 Selected Vibrational Assignments of LHDP molecule

Frequency cm^{-1}		Spectroscopic assignment	Force constant	Reduced mass
B3LYP	Experimental			
3641.0169	-	NH st	8.3194	1.0651
2990.9085	2991	C-H st	5.9790	1.0622
2854.0305	2861	NH ₃ asy st	5.6998	1.0372
1828.7112	1859	C=O st	23.9472	12.1539
1637.6173	1617	NH ₃ sy b	1.4493	1.0404
1587.4007	1588	NH ₃ asydef	1.5527	1.0865
1333.3448	1326	CH opb	1.2841	1.1555
1449.8902	1438	OH ipb	1.4083	1.5010
1161.6827	1163	CH ₂ roc	2.3333	2.7887
1276.3151	1281	OH ipb	1.0936	1.6023
922.8158	914	NH ₃ roc	7.2954	13.3571
835.2978	833	CH opb	0.4539	1.1042
724.7566	712	R opb	4.3985	11.8190
626.8864	626	O-H opb	3.4271	12.3284
548.2281	555	C-C ben	0.2126	1.2008
31.7170	-	CC ben	0.0026	4.3108

St-stretching; **syst**- symmetry stretching; **asy**st- asymmetry stretching;
ipb-in-plane bending; **opb**- out-of-plane bending; roc – rocking;
asydef – asymmetric deformation

The components of first order hyperpolarisability can be determined using the relation

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{j \neq i} (\beta_{ijj} + \beta_{jji} + \beta_{jii}) \quad (2)$$

Using the x,y and z components the magnitude of first order hyperpolarisability (β_{tot}) tensor can be calculated by the following equation

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (3)$$

The complete equation for calculating the first order hyperpolarisability from GAUSSIAN 03W output is given as

$$\beta_{\text{tot}} = (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \quad (4)$$

The β components of GAUSSIAN 03W output are reported in atomic units and the calculated values are converted into electrostatic units (1 a.u = 8.3693×10^{-33} esu). Hyperpolarisability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of 3D matrix can be reduced to 10 components due to Kleinman symmetry [5]. The calculated first order hyperpolarisability values for LHDP molecule are given in table 2. The calculated first order hyperpolarizability of LHDP is 3.18631×10^{-30} esu.

Table-2. Hyperpolarizability of LHDP in esu

Hyperpolarizability in esu	
β_{xxx}	-217.36375
β_{xyy}	-251.23383
β_{xyy}	-189.148803
β_{yyy}	-165.304903
β_{xxz}	103.2400168
β_{xyz}	-114.314853
β_{yyz}	161.5513002
β_{xzz}	-140.921474
β_{yzz}	1.7805245
β_{zzz}	-361.372294
β_{tot}	5.80467×10^{-30}

HOMO-LOMO Analysis

The interaction of two atomic (or) molecular orbitals produces two new orbitals. One of the new orbital is higher in energy than the original ones (the anti-bonding orbital) and one is lower (the bonding orbital). When one of the initial orbitals is filled with a pair of electrons (a Lewis base) and the other is empty (a Lewis acid), we can place the two electrons into the lower, energy of the two new orbitals. The “filled-empty” orbital interaction therefore is stabilizing. The highest energy occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the compound interact most strongly. HOMO Energy of LHDP is -0.312 a.u and LUMO Energy is -0.129 a.u. HOMO – LUMO energy Gap is found as -0.183 a.u.

IV. CONCLUSION

Non Linear optical LHDP is synthesized in the laboratory using suitable precursors. Its molecular structure is optimized to ground state energy using GAUSSIAN 03 programme package. Geometrical parameters of the candidate material are studied. Vibrational frequencies of the material are studied. Dipole moment of LHDP is in the range of its charge transferring ability. Hyperpolarizability and HOMO LUMO gap of the material is studied. Theoretical calculations show that LHDP is a good NLO material.

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