Molecular Structure, First-Order Hyperpolarizability and Homo-Lumo Studies of L - Asparaginium Picrate

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Abstract **- The geometric parameters and hyperpolarizabilities of a nonlinear optical material L-asparaginium picrate (LAsP) was investigated by density functional theory and presented. The compound crystallizes in the noncentro symmetric space group $P2_1$ of Monoclinic system. The first order hyperpolarizability (β) of this molecular system is calculated using B3LYP/6-31G (d,p) method on the finite-field approach. The calculation results also show that the LAsP molecule might have microscopic nonlinear optical behavior with non zero values. The optical absorption spectrum and second harmonic generation were investigated. The calculated HOMO and LUMO energies showed that charge transfer occurs within the molecule.**

Key words **- Molecular Structure, HOMO-LUMO and hyperpolarizability**

I. INTRODUCTION

Nonlinear optical (NLO) phenomena have been extensively studied over the last two decades; molecules exhibiting large hyperpolarizabilities have a strong NLO potential and could be used, under conditions for optoelectronics and a variety of optical devices [1, 2]. In the present work, LAsP was synthesized by slow evaporation method and the structural properties were calculated by DFT calculation. The experimental spectra are compared with calculated findings. Literature survey also reveals that to the best of our knowledge no DFT calculations have been reported yet. Therefore, the present investigation was undertaken to study the vibrational spectra of this molecule and to identify the various normal modes with greater wavenumber accuracy. In this context, the hyperpolarizability of the title compound was calculated in the present study.

II. SYNTHESIS OF LAsP

All the starting materials for synthesis of LAsP are purchased as AR grade (purity ≥ 99 %). Equimolar ratio of L-asparagine and picric acid is dissolved in deionized water (1:1). Synthesized salt of LAsP was obtained from the solution by evaporating the solvent and collecting the precipitate formed at the bottom of the container having the solution. The synthesized material was then purified by repeated crystallization process.

III. RESULTS AND DISCUSSIONS

Powder XRD Studies

The structural property of the grown LAsP is studied by X-ray powder diffraction technique. Powder X-ray diffraction studies were carried out, using Siemens D500 X-ray diffractometer with Cu K_α (λ = 1.5406Å) radiation. The samples were scanned for 2θ values from 10^0 to 40^0 at a rate of 2^0 /min. The diffraction pattern was indexed by least square fit method. The grown LAsP crystal belongs to monoclinic system with the non centrosymmetric $P2_1$ space group. The obtained cell parameters are a=10.365 Å, b=5.1618 Å, c=13.122 Å, $\alpha = \gamma = 90^0$, $\beta = 93.24°$ and V = 700.93Å^3.

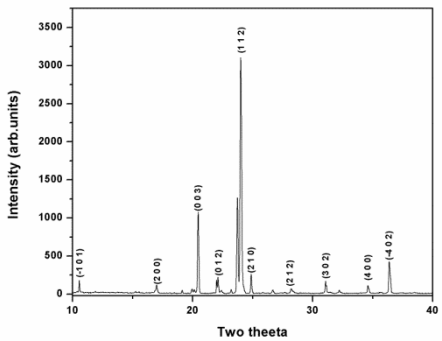

Figure 1. XRD Pattern of LAsP

Hyperpolarizability

The β values of LAsP compound was calculated by the DFT-B3LYP functional with the 6-31G (d, p) basis set [4]. In this context, the dynamic first hyperpolarizability of the title compound is also calculated in the present study. The first hyperpolarizability (β_o) of this novel molecular system is calculated using B3LYP/6-31G(d) method, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a 3×3×3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [5]. For LAsP β_{tot}= 15.3863 x 10^{-30} esu. A large value of the first hyperpolarizability is the prerequisite to behave as a good NLO material, and the important parameters influencing β generally are

(i) donor–acceptor system, (ii) nature of substituents, (iii) conjugated π system and (iv) the influence of planarity. The results also show that the compound studied in our research is a good NLO material due to its β value.

HOMO – LUMO

The calculations were done with the commonly used exchange-correlation functional B3LYP followed by a comprehensive analysis of the calculated highest-occupied and lowest-unoccupied Kohn-Sham orbital (HOMO and LUMO) energies. The basis set dependence of the DFT results shows that the economical 6-31+G basis set is generally sufficient for calculating the HOMO and LUMO energies (if the calculated LUMO energies are negative) for use in correlating with molecular properties.

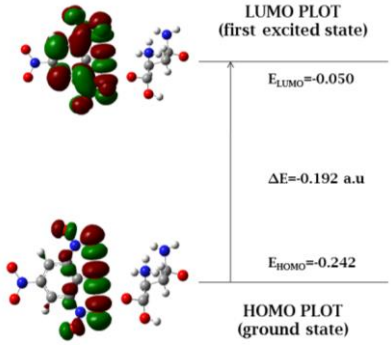

Figure 2. The atomic orbital compositions of the frontier molecular orbital for LAsP

On the basis of fully optimized ground-state structure, DFT/B3LYP/6-31G(d,p) calculations have been used to determine the low-lying excited states of LAsP. The calculated results involving the vertical excitation energies, oscillator strength (f) and wavelength are carried out and compared with measured experimental wavelength.

The HOMO-LUMO energy gap of LAsP was calculated at the B3LYP/6-31(d,p) level reveals that the energy gap reflect the chemical activity of the molecule and found to be -0.192 a.u. LUMO as an electron acceptor represents the ability to obtain an electron, HOMO represents the ability to donate an electron. All of the calculations were performed by using the Gaussian 03.

SHG Efficiency

The SHG efficiency of the grown crystal was measured by the standard Kurtz and Perry powder technique [6] using a fundamental beam of a Q–switched Nd:YAG laser with a wavelength of 1064 nm. To make relevant comparison with known SHG materials, KDP was also powdered and sieved into the same particle size range. The results obtained by this method shows that the SHG efficiency of LAsP sample is nearly 65.4 times more than that of KDP.

UV- Vis Spectrum

The UV-Vis absorption spectrum of the crystal was recorded in a wavelength range of 200 – 1100 nm and is shown in Figure 3. From the spectrum, it is seen that the UV cutoff occurs at 240 nm and there is no remarkable absorption in the entire region of the spectra. This is a favorable character for a NLO material.

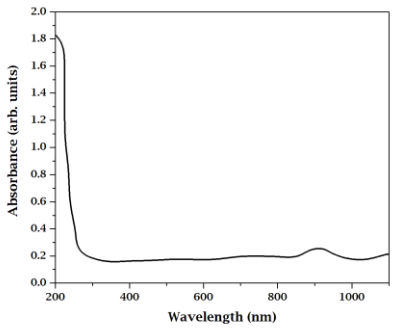

Figure 3. UV Vis NIR Spectrum of LAsP

IV CONCLUSIONS

Single crystals of LAsP were synthesized and grown from aqueous solution. The grown crystals were characterized by Powder XRD analysis. The study reveals that the grown crystals belong to monoclinic system. SHG measurement shows that the crystal has superior properties than KDP crystal. HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. Furthermore, first-order hyperpolarizability of the molecule shows that the title molecule is an attractive object for future studies of nonlinear optical properties.

REFERENCES

[1]. S. Senthil, S. Pari, P. Sagayaraj, J. Madhavan, Studies on the electrical, linear and nonlinear optical properties of Meta nitroaniline, an efficient NLO crystal,Physica B, Vol.404, pp 295, 2009.

[2]. S. Senthil, S. Pari, R. John Xavier, J. Madhavan, Linear and nonlinear optical properties of N-(3-nitrophenyl) acetamide

single crystals, Optik, Vol.123, pp 104, 2011.
[3]. S. Aruna, G. Bhagavannarayana, P. Sagayaraj, Investigation on the physicochemical properties of nonlinear optical (NLO) single crystal: L-histidinium dinitrate, J. of Crystal Growth, Vol.304, pp – 184, 2007.
[4]. Frisch M.J, Trucks G.W, Schlegel H.B, Scuseria G.E, Robb M.A, J.R. Cheeseman J.R, Montgomery Jr J.A, Vreven T, Kudin K.N, Burant J.C, Millam J.M, Iyengar S.S, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G,.Rega N, Petersson G.A, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox J.E, Hratchian H.P, Cross J.B, Adamo C, Jaramillo J, Gomperts R, Stratmann R.E, Yazyev O, Austin A.J, Cammi R, Pomelli C, Ochterski J.W, Ayala P.Y, Morokuma K, Voth G.A, Salvador P, Dannenberg J.J, Zakrzewski V.G, Dapprich S, Daniels A.D, Strain M.C, Farkas O, Malick D.K, Rabuck A.D, Raghavachari K, Foresman J.B, Ortiz J.V, Cui Q, Baboul A.G, Clifford S, Cioslowski J, Stefanov B.B, Liu G, A.Liashenko, Piskorz P, Komaromi I, Martin R.L, Fox D.J, Keith T.,.Al-Laham M.A, Peng C.Y, Nanayakkara A, Challacombe M, Gill P.M.W, Johnson B, Chen W, Wong M.W, Gonzalez C, Pople J.A, Gaussian 03, Revision C.02, Gaussian Inc.,Wallingford, CT, 2004.
[5]. D. A. Kleinman, Nonlinear dielectric Polarization in Optical Media, Phys. Rev., Vol. 126, 1977.
[6]. S. K. Kurtz, T. T. Perry, A Powder Technique for the Evaluation of Nonlinear Optical Materials, J. Appl. Phys.,Vol .39, pp 3798, 1968.