UV-Vis, HOMO-LUMO AND HYPERPOLARIZABILITY OF L-PHENYLALANINE L-PHENYLALANINIUM-BENZOIC ACID

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Abstract - Nonlinear optical single crystal of L-phenylalanine L-phenylalaninium-benzoic acid (LPB) was grown by slow evaporation technique. The grown crystal was subjected to optical characterization by UV-Vis techniques. DFT calculations predicted first order hyperpolarizability of LPB as 4.48715 x 10^{-30} esu, which suggests that the title compound is an attractive material for non-linear optical applications. The calculated HOMO-LUMO energies show that charge transfer occurs within the molecule. The SHG efficiency was measured using the Kurtz powder technique. The efficiency was found to be higher than that of KDP.

Keywords – LPB, UV, DFT

1 INTRODUCTION

In recent decades, more attention has been paid towards organic nonlinear optical materials because of their wide transparency in UV and visible region, high nonlinear susceptibility, high laser damage threshold and fast response than the commercially available inorganic materials. By molecular engineering, one can develop many organic crystals displaying better nonlinear optical properties than the inorganic materials, in particular for Second Harmonic Generation (SHG) [1, 2]. In this present communication, the synthesis and growth of LPB from its aqueous solution by slow evaporation method has been reported. As an organic molecule LPB has its own advantage over the conventional KDP single crystal. The title molecule is exposed to DFT analysis, first order hyperpolarizability studies and second harmonic generation efficiency measurements. To the best of our knowledge no DFT calculations have been reported yet. Therefore, the present investigation was undertaken to study the absorption. In this context, the hyperpolarizability of the title compound was also calculated.

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2 EXPERIMENTAL DETAILS

Single crystals of LPB were grown from L-phenylalanine and benzoic acid taken in stoichiometric ratio dissolved in aqueous solution and grown by slow solvent evaporation technique. UV-Vis absorption spectrum of the compound was recorded in the range 200 nm – 1100 nm. The nonlinear optical property of the grown single crystal is tested by passing the output of Nd:YAG Quanta ray laser through the crystalline powder samples of LPB and the reference material KDP.

3 OPTICAL STUDIES

The optical properties of a material are important, as they provide information on the electronic band structures, localized states and types of optical transitions. Figure 1 shows the optical absorption spectrum of LPB. The good absorption property of the crystal in the entire visible region suggests its suitability for second harmonic generation. From the spectrum it is observed that the UV cut-off wavelength lies around 250 nm.

The lower cutoff wavelength lies around 200 nm which is due to the π–π^* transition in this compound. Using Tauc's relation, a graph has been plotted to estimate the band gap value. Figure 2. shows the plot of $(\alpha h\nu)^2$ versus hv, where α is the optical absorption coefficient and hv is the energy of the incident photon. The direct energy gap (E_g) is determined by extrapolating the straight line portion of the curve to $(\alpha h\nu)^2 = 0$. From this drawing, E_g is found to be 4.91 eV. Thus confirming the wide band nature of aminoaicd based optical materials.[3].

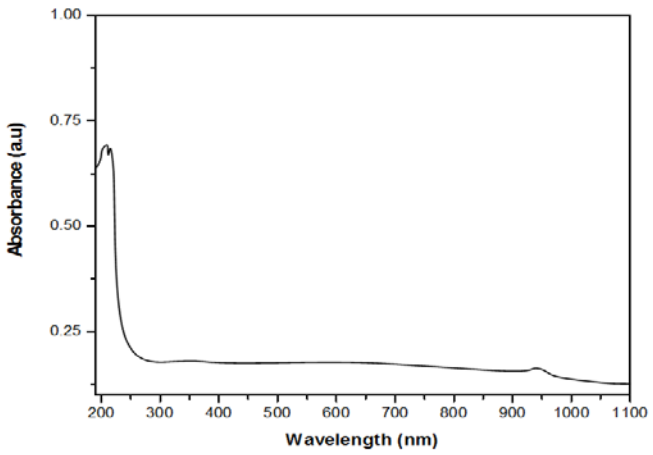


Figure 1. Optical absorption spectrum of LPB

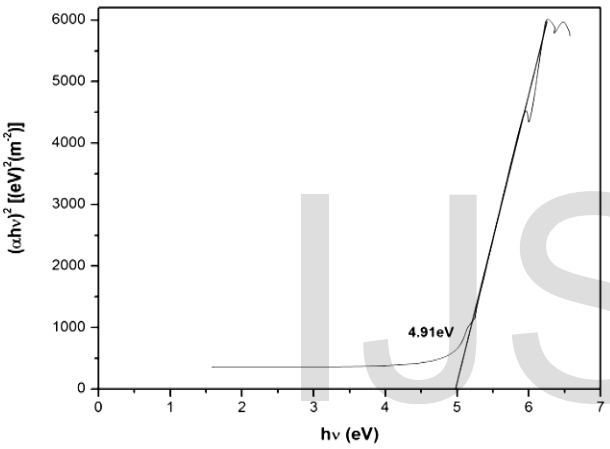


Figure 2. Tauc's plot of LPB

4 HYPERPOLARIZABILITY STUDIES

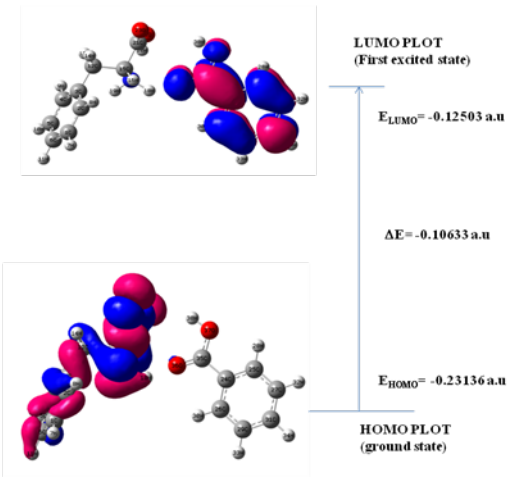
The β values of LPB compound was calculated by the DFT-B3LYP functional with the 6-31G (d, p) basis set [4]. In this context, the dynamic first hyperpolarizability of the title compound is also calculated in the present study. The first hyperpolarizability (β_o) of this novel molecular system is calculated 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]. 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 is a good NLO material due to its β values.

Table 1 Hyperpolarizability in esu of LPB molecule

β_{xxx}	7.2194841
β_{xxy}	47.7839117
β_{xyy}	156.7094198
β_{yyy}	300.6206897
β_{xxz}	-38.7978718
β_{xyz}	42.7360532
β_{yyz}	26.9268426
β_{xzz}	49.0220072
β_{yzz}	24.4667482
β_{zzz}	-309.174049
β_{tot}	4.48715×10^{-30}

5 HOMO-LOMO ANALYSIS

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.



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 LPB. 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 LPB was calculated at theB3LYP/6-31(d, p) level reveals that the energy gap reflect the chemical activity of the molecule and found to be

-0.10633 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.

6 NLO STUDIES

The powder sample, with an average particle Size of 50 - 150 μm was illuminated using a Q-switched mode-locked Nd^{3+}:YAG laser of pulse width 8 ns at a wavelength of 1064 nm and 10 Hz fundamental radiation. In the SHG efficiency measurements, microcrystalline material of KDP of the same particle size was used for comparison. A laser input of 10.8 mJ was passed through LPB and the reference material KDP. It is found that the efficiency of LPB 1.6 times greater than that of KDP [6].

7 CONCLUSION

Good quality single crystal of LPB was grown by slow solvent evaporation technique. Density functional theory (DFT) computations using (B3LYP) level with 6-31 G (d, p) basis set gave the optimized structure of LPB molecule. Molecular energy gap of LPB was found as -0.10633au by HOMO-LUMO analysis. The low HOMO - LUMO energy gap confirmed the charge transfer within the molecule. Optical absorption spectrum was recorded for the given crystal and it is found that it has minimum absorption in the entire visible region. This nonlinear optical analysis reveals the NLO behavior of the material.

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