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Structural and spectroscopicalstudiesonL-phenylalanine L-phenylalaninium-benzoic acid

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Abstract :- The Infrared spectrum of L-phenylalanine L-phenylalaninium-benzoic acid (LPB) was recorded and analyzed in the region 4000–400 cm^{-1}. Optimized geometrical structures and harmonic vibrational frequencies have been computed by the B3 based (B3LYP) density functional method using 6-31+G (d, p). The calculated first hyperpolarizability is comparable with the reported value of similar structures and may be an attractive object for further studies on non-linear optics. The geometries and normal modes of vibration obtained from DFT method are in good agreement with the experimental data. The calculated HOMO and LUMO energies show that charge transfer occurs within molecule.

Keywords: LPB, FT-IR, Hyperpolarizability, HOMO, LUMO.

Introduction

Density Functional Theory (DFT) is one of the most widely used methods for "ab initio" calculations of the structure of atoms, molecules, crystals, surfaces, and their interactions. The added esteem of nonlinear optical materials over lasers and electro-optics became preponderant from the early days of lasers. NLO materials endow the expansion of the circumscribed spectral regime of lasers [1-3]. Experimental measurements and theoretical calculations on molecular hyperpolarizability become one of the key factors in the second-order NLO materials design. Theoretical determination of hyperpolarizability is quite useful both in understanding the relationship between the molecular structure and nonlinear optical properties. Therefore, the present investigation was undertaken to study the vibrational spectrum of this molecule and to identify the various normal modes with greater wave number accuracy. Ab initio and DFT calculations have been performed to support our wave number assignments.

Synthesis

Single crystal of LPB was grown from L-phenylalanine L-phenylalaninium and benzoic acid taken in the equimolar ratio and dissolved in aqueous solution and kept for slow solvent evaporation. Optically clear and well-shaped crystals were obtained.

Computational details

Ab initio molecular calculations were performed using the Gaussian03W (8) program package, Further geometry optimizations and vibrational frequencies of the favoured conformers were carried out at basic DFT level using B3LYP-6-31G(d,p) [4].Finally, the calculated normal mode vibrational frequencies provide thermodynamic properties also through the principles of statistical mechanics. At the optimized structure of the examined species, no imaginary wavenumber modes were obtained, proving that a true minimum on the potential surface was found.

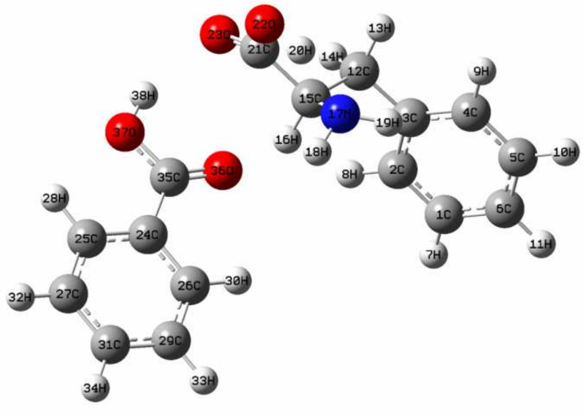

Figure 1. Optimized Structure of LPB

FT-IR Analysis

The FT-IR spectrum of LPB was recorded using BRUKER IFS–66V spectrometer in the range between 4000 and 400 cm^{-1}. The experimental and theoretical middle IR spectrum of LPB is shown in table 1 and Figure 2 and 3 respectively.The broad envelope between 3400 and 2500 cm^{-1} includes absorption of stretching bands due to NH_3^+ion of the amino acid. The NH_3^+ asymmetric and symmetric stretching vibrations are positioned at 3290 and 2598 cm^{-1} respectively. In our present investigation a strong band observed in FT-IR spectrum at 620 $cm^{-1}$is assigned to O–H out-of-plane deformation, the theoretically computed value by BLYP and B3LYP also shows the same kind of vibrations in the range 622.43cm^{-1}.The asymmetric and symmetric C–H vibration for methyl group is usually occurring in the region between 2975 and 2920 cm^{-1}[5]. In this molecule, the C–H vibration frequency is observed at 2960 cm^{-1} and DFT is 2970.4 cm^{-1}.Strong carbonyl absorption at 1725 cm^{-1} identifies the COOH and COO^- groups of the compound. For the title compound, the C=O stretching band is observed at 1725 cm^{-1} and at 1758cm^{-1} theoretically. Further strong band observed at about 1217 cm^{-1} is due to C-COO^-stretching. The presence of L-phenylalanine ions in the crystal structure is reflected in the bands of the COO^- wagging (555 cm^{-1}).

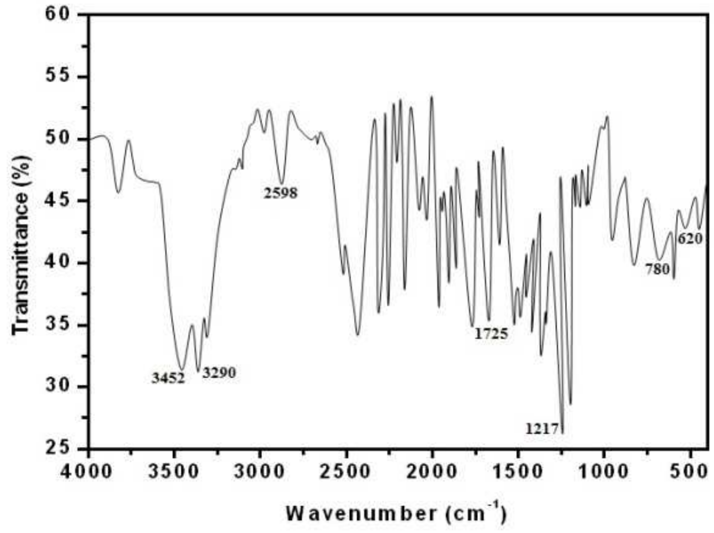

Figure 2. Observed FTIR spectrum of LPB crystal.

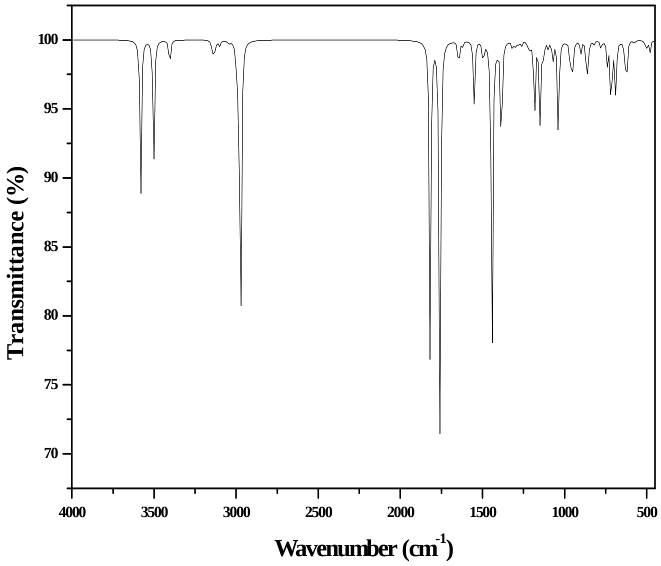

Figure 3. Calculated FTIR spectrum of LPB crystal

Table 1.Experimental and Calculated vibrational frequencies of LPB

Wave number (cm^{-1})	**6-31 G (d, p)**	**Assignment**
3452	3404.35	O-H stretch of COOH
3290	3148.09	NH_3^+asymmetric stretching
2960	2970.4	CH vibration
2598		NH_3^+ symmetric stretching
1725	1758.63	C ═ O stretching vibrations
1598	1550.66	COO^- asymmetric stretching
1504	1496.41	NH_3^+symmetric vibration
1480	1495	O-H symmetric stretching
1417	1420.74	COO^- symmetric stretching
1217	1214.72	C- COO^- stretching
780	777.06	NH_2 rocking
703	691.199	NH_2 Out-of-plane bending
620	622.43	OH out-of-plane deformation
555	575.498	COO^- Wagging

Hyperpolarizability

In the presence of an applied electric field, the energy of a system is a function of the electric field, and the first hyperpolarizability is a third rank tensor that can be described by a 3 x 3 x 3 matrix. The first order static hyperpolarizability is also significantly affected by the basis set in calculation. The 27 components of 3D matrix can be reduced to 10 components because of the Kleinmann symmetry [6]. The matrix can be given in the lower tetrahedral format. The calculated first order hyperpolarizability (β_{total}) of LPB is 4.48715 x 10^{-30}esu.

HOMO–LUMO band gap

Owing to the interaction between HOMO and LUMO orbital of a structure, transition state transition of $\pi - \pi^*$ type is observed with regard to the molecular orbital theory [7]. Therefore, while the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability for structures. According to B3LYP/6-31G (d, p) calculation, the energy band gap (ΔE) (translation from HOMO to LUMO) of the molecule is about -0.10633au.

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. FT-IR studies identify the functional groups present in the compound. The nonlinear optical analysis reveals the NLO behavior of the material.

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