

Vibrational, Spectral Investigation of Nonlinear Optical L-Isoleucine D-Alanine: Experimental and Theoretical Confirmation

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Abstract. Optically transparent amino acid based nonlinear crystal of L-Isoleucine D-Alanine (LIDA) was grown from its aqueous solution by slow solvent evaporation technique. The material was studied in-depth by using vibrational spectrum and density functional theory (DFT). The Fourier transform infrared (FT-IR) spectrum was recorded in the range 4000 cm^{-1} – 450 cm^{-1} . Meanwhile, the DFT computations are performed at B3LYP/6-31G+ (d, p) level to obtain equilibrium geometry, vibrational wave numbers and first hyperpolarizability. The scaled theoretical wave numbers are also shown to be in good agreement with experimental data. From the UV-Vis spectrum the transmittance abilities of the crystal were studied. The band gap of the material was determined from the Tauc plot.

1. INTRODUCTION

In the modern world, the development of science in many areas has been achieved through the growth of single crystals. Crystal growth of organic materials has been recently attracting scientific attention in the search of new nonlinear optical materials. Many organic materials have been found to have greatly nonlinear or optoelectrical properties than inorganic substances [1]. Some organic compounds exhibit large NLO response, in many cases, order of magnitude larger than widely known inorganic materials. They also offer the flexibility of molecular design and the promise of virtually an unlimited number of crystalline structures. Amino acids are the famous organic materials which can play a role in nonlinear optics as they contain proton carboxylic acid (COOH) group and the proton acceptor amino (NH₂) group. Considerable efforts have been made on the amino acid mixed complex crystals in order to make them suitable for device fabrications. L-Isoleucine is one of the proteinogenic amino acids that aids in the production of protein. It is a branched chain amino acid (BCAA) that is classified as a hydrophobic amino acid. One of its main benefits is increased strength and rapid muscle repair when combined with other amino acids. It is also beneficial for children and teens that are in their growing years because it is vital for healthy growth. Alanine is an efficient organic NLO compound under the amino acid category. It is the simplest amino acids with an asymmetric carbon atom. Alanine and DL-Alanine are the usually available forms of alanine. In this chapter, we tried to report the growth and characterization of L-Isoleucine D-Alanine (LIDA) single crystal.



2. EXPERIMENTAL DETAILS

The LIDA compound was synthesized by the direct combination of L-Isoleucine and D-Alanine in distilled water at room temperature. The synthesized compound was further purified by repeated recrystallization. Purified salt of LIDA were collected and further used for bulk single crystal growth. The grown crystal is shown in the figure.1 of size measuring $8 \times 5 \times 7 \text{ mm}^3$. Finely crushed powder of LIDA crystal was subjected to powder X-ray diffraction analysis using $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. LIDA crystal has a monoclinic structure and the lattice parameters are tabulated in Table.1.



Figure.1 Photograph of as grown LIDA single crystal

Table 1. Crystal data

Crystal data	
Empirical formula	$\text{C}_9\text{H}_{20}\text{N}_2\text{O}_4$
Crystal System	Monoclinic
Space Group	P2_1
a(Å)	9.8944
b(Å)	4.7425
c(Å)	12.9045
$\beta(^{\circ})$	93.374

3. RESULTS AND DISCUSSION

3.1 Vibrational Spectral Analysis

The main objective of the vibrational analysis is to find vibrational modes connected with specific molecular structures of the compound. The best possible fitting was done between the calculated and experimental vibrational wavenumbers. The title molecule consists of 35 atoms, hence undergoes 99 normal modes of vibrations. These normal modes of vibrations are further classified into 67 in-plane vibrations and 32 out plane vibrations. The experimental FT-IR spectrum is as shown in Figure.2.

NH_3^+ group vibration

In zwitterionic molecules, theoretically the NH_3^+ symmetric stretching band appears at the value $3085.4737 \text{ cm}^{-1}$ and experimentally appears at the value 3088 cm^{-1} respectively [2]. The NH_3^+ symmetric deformation theoretically appears at $1537.3389 \text{ cm}^{-1}$ [3].

Carboxylate group vibration

The asymmetric and symmetric stretching modes of carboxylate ion vibrations theoretically occur at 1557.9300 cm^{-1} and 1451.4792 cm^{-1} respectively [4]. COO^- deformations theoretically occurs in the region 528.6117 cm^{-1} - 582.6304 cm^{-1} and experimentally present at the value 539 cm^{-1} [5]. The COO^- deformation coupled with rocking mode appears theoretically at the value 675.0159 cm^{-1} - 740.3881 cm^{-1} in IR as a very strong band.

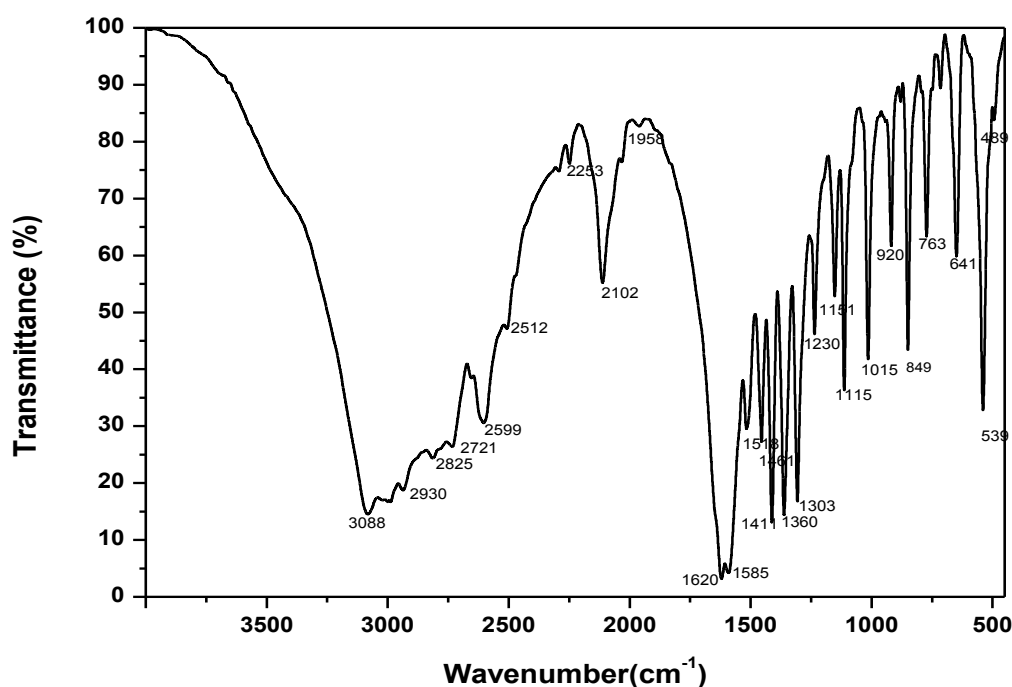


Figure 2. Experimentally obtained FT-IR spectrum of LIDA

C-N vibrations

C-N stretching absorptions are assigned theoretically in the region 1271.3646 cm^{-1} - 1383.5730 cm^{-1} and experimentally at 1303 cm^{-1} , 1360 cm^{-1} for primary aromatic amine with nitrogen directly on the ring.

NH₂ vibrations

The NH_2 asymmetric stretching vibrations theoretically give rise to a strong band in the region 3404.9086 cm^{-1} - 3429.2699 cm^{-1} and the symmetric NH_2 stretching is observed as weak band in the region 3152.8348 cm^{-1} - 3160.8503 cm^{-1} theoretically.

O-H vibrations

The O-H out-of-plane bending mode for the free molecule lies in the region 5.0714 cm^{-1} - 289.9627 cm^{-1} theoretically and it is beyond the infrared spectral range of the present investigation. However, for the associated molecule the O-H out-of-plane bending mode lies theoretically in the

region 528.6117 cm^{-1} - 675.0159 cm^{-1} and experimentally at 539 cm^{-1} in both intramolecular and intermolecular associations, the frequency is at a higher value than in free O-H.

COOH vibrations

The carbonyl group is contained in many different classes of compounds, for which a strong absorption band due to C=O stretching vibration is observed theoretically in the range of 1557.9300 cm^{-1} - 2086.7851 cm^{-1} . The vibrational assignments are presented in Table.2.

Table 2. Vibrational Assignments of LIDA Molecule

No	Wavenumber (cm^{-1})		Spectroscopic assignment	Force constant	Reduced mass
	B3LYP	Expt.			
1.	528.6117	539	COO ⁻ def	0.3631	2.2058
2.	843.3942	849	C-N abs	0.5149	1.2286
3.	932.3841	920	NH ₃ roc	1.0113	1.9744
4.	1024.5942	1015	NH ₂ t	0.7400	1.1965
5.	1109.4946	1115	OH ipb	1.1096	1.5299
6.	1138.4561	1151	CH ₂ roc	1.4700	1.9250
7.	1233.3331	1230	COO ⁻ st & b	1.3043	1.4553
8.	1309.8000	1303	COO ⁻ st & b	1.6224	1.6051
9.	1362.7537	1360	COO ⁻ st & b	1.8737	1.7125
10.	1421.2563	1411	C-H b+ C=C st	2.1903	1.8403
11.	1460.9092	1461	C-H b+ C=C st	4.0324	3.2067
12.	2929.0913	2930	CH ₂ st+ C-H st	5.3970	1.0677
13.	3085.4737	3088	NH ₃ ⁺ sym st	5.9061	1.0529

def- deformation, st- stretching, abs- absorption, st & b-stretching & bending, t- twisting, sym st- symmetric stretching.

3.2 Molecular Geometry and Hyperpolarizability

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 software package. Optimized structure was confirmed to minimum energy conformations. The optimized molecular structure of the isolated LIDA is shown in Figure.3. The second-order polarizability or first hyperpolarizability was calculated by B3LYP using 6-31G (d, p) basis set on the basis of the finite-field approach. Theoretical calculations on molecular hyperpolarizability become one of the key factors in the second-order NLO materials design. Theoretical determination of hyperpolarizability provides a guideline to experimentalists for the design and synthesis of organic NLO materials. Nonlinearity in organic chromophores can be synthetically modulated by varying the composition or length of conjugated p-systems, and by evaluating the effects of various electron-donor and electron-acceptor groups. They determine not only the strength of molecular interactions (long-range interaction, dispersion force, etc.) and the cross

sections of different scattering and collision process but also the NLO properties of the system. The hyperpolarizability values are listed in Table.3.

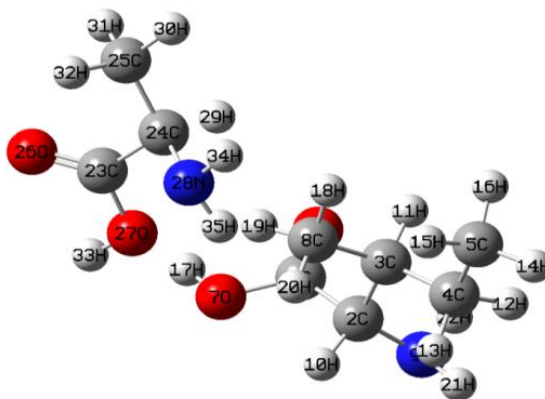


Figure 3. Atomic numbering for ab initio computations of LIDA molecule

Table 3. Hyperpolarizability of LIDA in esu

β_{xxx}	-275.705
β_{xxy}	-109.758
β_{xyy}	-187.947
β_{yyy}	-9.47754
β_{xxz}	-0.0259567
β_{xyz}	-0.00107375
β_{yyz}	-0.0120082
β_{xzz}	6.55646
β_{yzz}	-30.2164
β_{zzz}	0.0216665

3.3 Optical Absorption Spectrum

In order to determine the optical transmission characteristics of the grown crystal UV-Vis spectrum was recorded on the cut and polished grown sample. The UV-Vis spectral absorption was studied using a Varian Cary 5E UV-Vis-NIR spectrophotometer with a single crystal of 6mm thickness in the range of 200–800nm. The recorded spectrum is shown in Figure. 4 and 5. The crystal has sufficient transmission in the entire visible and IR region. The lower cut off wavelength is around 240 nm. From the absorbance energy band gap was evaluated. The E_g could be estimated from the plots of $h\nu$ versus $(\alpha h\nu)^2$.

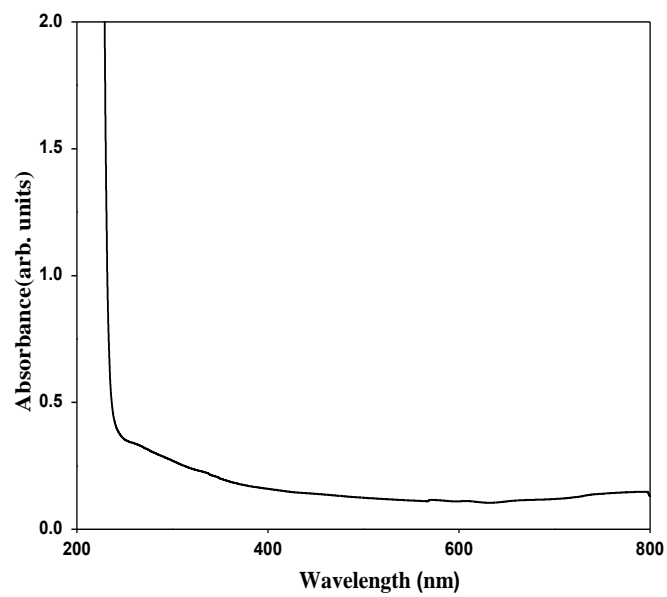


Figure 4. Optical absorption spectrum of LIDA crystal

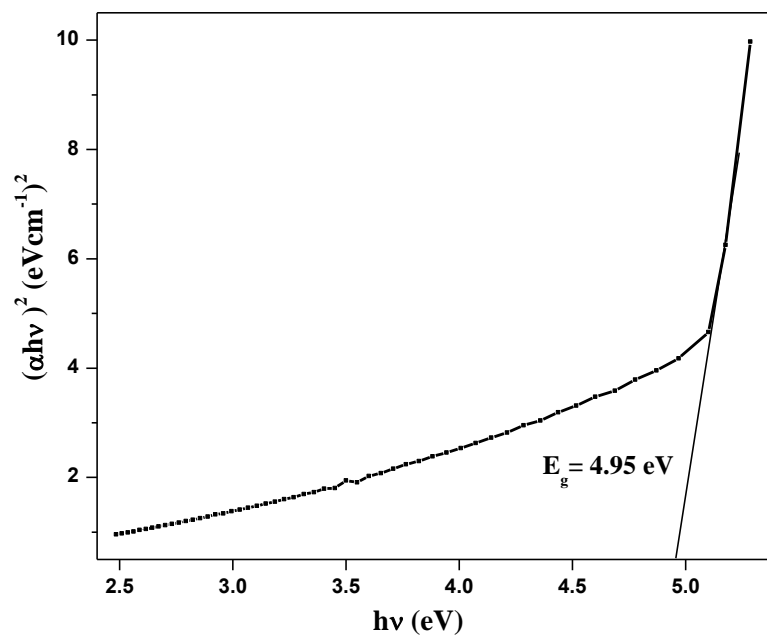


Figure 5. Optical band gap of LIDA crystal

4. Conclusion

Single crystal of L-Isoleucine D-Alanine (LIDA) was grown successfully by slow evaporation technique. Optimized structure of the isolated LIDA molecule obtained by DFT calculations give the minimum energy state. Existence of strong hydrogen bond in the donor acceptor coupling was understood from bond lengths. First order hyperpolarizability of LIDA is calculated as $4.024860812 \times 10^{-30}$ esu and found useful in molecular designing. Theoretical and experimental spectroscopic studies exemplify the presence of various functional groups in the molecule. The UV-Vis spectrum reveals minimum absorption in the entire visible region.

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