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Graphical abstract



Structural and spectroscopic investigations of nonlinear optical crystal Lphenylalanine fumaric acid by DFT calculations

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Abstract

The title compound L-phenylalanine fumaric acid has been synthesized in slow evaporation solution growth technique. The crystallinity of the crystal is confirmed by powder X-ray diffraction studies. Complete vibrational analysis and optimized molecular structure is obtained using density functional theory calculations. The vibrational contribution of each normal mode is figured out by calculating potential energy distribution with the aid of vibrational energy distribution analysis (VEDA 4) program. Experimental FT-infrared and FT-Raman spectra are recorded and analyzed. The second harmonic generation (SHG) efficiency of the grown crystal is measured by Kurtz – Perry technique. The calculated first hyperpolarizability and the highest occupied molecular orbital (HOMO) - lowest unoccupied molecular orbital (LUMO) energies confirm the nonlinear optical activity of the compound. The theoretical and experimental cutoff wavelength corresponding to electronic transitions are obtained. The most important hyper conjugative interactions leading to the stability and intramolecular charge transfer of the system is elucidated by natural bond orbital analysis. Information regarding the charge density distribution and chemical reactivity sites of the compound has been obtained by mapping molecular electrostatic potential.

Keywords: DFT; SHG; Charge transfer; NBO; Raman; MEP.

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1. Introduction

Nonlinear optical (NLO) crystals having good stability, high transparency in the visible region and superior nonlinear susceptibilities are noteworthy due to their influence on the development of laser technology and optoelectronic industry. In recent years, amino acid complexes having chiral symmetry along with zwitterionic nature due to the occurrence of donor acceptor groups have been identified to have diverse application in science and industry [1-4]. Several L-phenylalanine crystals have been recognized as efficient NLO organic crystals due to their high transparency in the range 380-800 nm and high damage threshold [5-11]. L-phenylalanine is a naturally occurring aromatic, hydrophobic and α -amino acid produced by the biological breakdown of protein in the body. It includes a phenyl ring having a side chain substituted with an electron withdrawing -COOH moiety and electron donating NH₂ moiety. The occurrence of these donor-acceptor groups influences the optical proficiency of the crystals [12]. The wide transparency of organic acids makes them an excellent associate for amino acids to fabricate highly efficient nonlinear optical materials [13,14].

Theoretical studies of structural dependence on NLO properties are analyzed and normal modes of vibration of L-phenylalanine fumaric acid (PAF) are studied. First order hyperpolarizability, molecular electrostatic potential and Mulliken charges obtained by density functional theory level calculation are utilized to explore the molecular dynamics and chemical behavior of PAF.

2. Materials and Methods

2.1 Sample preparation

Transparent, colourless crystals of PAF has been prepared from the saturated aqueous solution of L-phenylalanine and fumaric acid in 1:1 ratio as described by Alagar *et al.* [15]. The resulting needle like crystal was repeatedly crystallized in double distilled water to obtain clear crystals within 2 weeks.

2.2 Powder X-Ray diffraction measurement

The powdered sample of PAF crystal was subjected to Bruker D8 advanced powder X-ray diffractometer (PXRD) with Cu K α radiation of 40 kV, 30 mA. The specimen was scanned for the angular range 20-80° 2 theta with the step size 0.0289°. The recorded spectrum is given in Fig. 1. The PXRD data indicates that, PAF belongs to triclinic crystal system in P1 space group. Lattice parameters of PAF are a=5.7144 Å, b=11.5489 Å, c=11.6149 Å and cell angles are α =67.6971°, β =81.1306°, γ =79.3863°. Cell volume, V=694.048 Å³. All these parameters go in agreement with the reported structural data and confirms the identity of the grown crystal [15]. The sharp nature of the peak indicates the purity and crystallinity of the crystal grown in the laboratory.

2.3 Spectroscopic measurements

FT-infrared (FT-IR) spectrum of the grown sample is analyzed with compact Spectrum two Lit A of Perkin Elmer. FT-IR spectra of the title compound in KBr pellet was recorded in the range 4000 - 400 cm⁻¹ at a resolution of 0.5 cm⁻¹. The NIR-FT Raman spectrum of LPF crystal was taken between 3500-50 cm⁻¹ using Bruker RFS 27 stand alone FT-Raman spectrophotometer which uses 1064 nm Nd:YAG laser source having 100 mW power. Ge-diode cooled with liquid nitrogen is used as detector. The spectral resolution is 2 cm⁻¹. The UV-visible spectrum was recorded in the range 200-500 cm⁻¹ in water solvent, using Jasco V-650 high resolution UV-visible spectrophotometer with double beam optics and photomultiplier tube detector. Resolution of the measured spectrum is 1.0 nm.

2.4 Second harmonic generation analysis

The grown crystal of PAF was graded with a standard sieve to reduce the particle size (r) to $150 < r < 180 \ \mu m$. Q switched high energy Nd:YAG laser having an incident wavelength of 1064 nm with a repetition rate of 10 Hz is used for the SHG measurement by powder reflection technique [16]. 95% of the fundamental laser intensity was focused on to the sample and the remaining 5% intensity was utilized as a reference to control fluctuations in incident beam. The experimental second harmonic intensity deviation coming out from the sample as a function of the fundamental intensity is plotted in Fig. 2. The PAF sample produced an output energy of 8.36 mJ which is 0.94 times that of potassium dihydrogen phosphate (KDP).

3. Computational techniques

All the quantum chemical computations performed in the present study is achieved using Gaussian '09 program package [17]. The hybrid exchange functional Becke three Lee-Yang-Parr (B3LYP) is utilized along with the basis set 6-31G(d) for obtaining structural optimization and harmonic frequency calculation. The normal mode frequencies obtained are real and establish that the optimized structure corresponds to a true local minimum. The stereo electronic interactions are interpreted by NBO 3.1 program incorporated in Gaussian '09 program at density functional theory (DFT) level. The quantitative explanation of normal mode contributions of the theoretical frequencies obtained from the potential energy distribution (PED) assignment is

completed using vibrational energy distribution analysis program (VEDA 4) [18]. The group contribution greater than or equal to 10% to each normal mode of vibration is interpreted after repeated optimization. The theoretical IR and Raman spectra simulated by Gaussian calculations have been plotted with full width at half maximum (FWHM) of 10 cm⁻¹ using pure Lorentzian band shapes. At the same time simulated Raman spectra is plotted with computed Raman activities (*Si*) converted to relative Raman intensities (*Ii*) by means of Eq. (1) obtained from the basic theory of Raman scattering [19, 20]. In Eq. (1) v₀ is the exciting frequency in cm⁻¹, v_i is the vibrational wavenumber of the ith normal mode, h, c and k are universal constants, and 'f' is the suitable scaling factor suitably commonly chosen for all the peak intensities.

$$I_{i} = \frac{f(v_{o} - v_{i})^{4} S_{i}}{v_{i} \left[1 - \exp\left(\frac{-hc v_{i}}{kT}\right)\right]}$$
(1)

Experimental and simulated IR and Raman spectra are depicted in Fig. 4 and Fig. 5 respectively for visual comparison. The structural optimization is achieved by iteratively solving the self-consistent field equation. This optimized molecular geometry produced 3N-6 positive frequencies thus ensuring a minimum on the potential energy surface. The systematic errors of calculated vibrational wavenumbers produced by incomplete basis set, ignoring anharmonicity and electron correlation were corrected by a scaling factor 0.9613 [21-23].

The components of the hyperpolarizability tensor calculated by density functional theory (DFT) method for the title compound are given in Table S1 (Supporting information). The components of the first hyperpolarizability are calculated according to Thanthiriwatte and Silva [24] by keeping the center of mass of the compound as the origin of the Cartesian coordinate

system [24-25]. The first order hyperpolarizability of PAF is calculated as 2.79×10^{-30} esu which is 4 times greater than the standard reference material KDP for which β_{tot} is 6.85×10^{-31} esu [7].

4. Results and Discussion

4.1 Optimized geometry

The structural optimization of the PAF molecule was achieved using Gaussian '09 program package. The optimized geometrical parameters obtained by DFT method using B3LYP functional are tabulated in Table 1 and the optimized structure is given in Fig. 3. The magnitude of bond angle O_{22} - C_{21} - O_{23} has enhanced by 5.83° compared to the experimental data [15] due to the intramolecular hydrogen bonding of O_{23} atom with H₂₄ atom of aliphatic fumaric acid. The lowering of bond angle C_{15} - C_{21} - O_{23} (112.15°) compared to that of C_{15} - C_{21} - O_{22} (117.45°), and elongated bond length of C_{21} - O_{23} compared to that of C_{21} - O_{22} is due to the intramolecular hydrogen bonding is affirmed by the decrease in O_{23} ···H₂₄ distance and increase in bond length of O_{25} -H₂₄ as well as C_{21} - O_{23} . The increase in O_{22} - C_{21} - O_{23} bond angle also supports the above inference. Likewise, there exists strong N-H···O interaction between N₁₇ and O₂₇ which is reflected in the lengthening of C_{26} - O_{27} , N₁₇-H₂₀ bonds and short distance between H₂₀···O₂₇. Lengthening of these bonds is due to the hyperconjugative interaction between lone pair orbital LP1 (O₂₇) and $\sigma^*(N_{17}$ -H₂₀) [26]. The occurrence of these two hydrogen bonded interactions gives increased stability for the system.

- Position for Figure 1
- Position for Figure 2
- Position for Figure 3

• Position for Table 1

4.2 Natural Bond Orbital and "bond bending" Analysis

For the analysis of electronic wavefunction, natural bond orbital (NBO) method is used by NBO 3.1 program [21]. The NBO analysis incorporates a collection of mathematical procedures to describe wavefunction in terms of Lewis to non-Lewis form of contributions. The most significant exchanges among donor Lewis type NBOs and acceptor non-Lewis NBOs are reported in Table 2. The quantitative contribution of s and p-character, occupancy of natural bonds and lone pairs, are calculated and are given in Table 2. Stabilization energy ΔE_{ij} is evaluated using second order perturbation theory as proposed by Reed *et.al.* [22].

Stability of the donor-acceptor interaction is observed by the amount of electron density delocalization among the bonding and antibonding NBOs. The strong intramolecular O-H^{...}O hydrogen bonding and charge delocalization is reflected in the stabilization energy E^2 of LP (O₂₃) to antibonding H₂₄-O₂₅. The electron density (ED) value (0.03149 e) of the antibonding $\sigma^*(H_{24}-O_{25})$ is a measure of intramolecular charge delocalization and hence the weakening of the bond marked by the elongation of bond length H₂₄-O₂₅. The stabilization of the system is achieved by hyperconjugative orbital overlap interaction between π (C-C) and π^* (C–C) of the phenyl ring.

The hyperconjugative interaction between lone pair LP₁ (O₂₇) with $\sigma^*(N_{17}-H_{20})$ is of much importance because of the decreased electron density of non-Lewis orbital, and its effect on bond length and molecular stability. The elongation of N₁₇-H₂₀ bond length is due to the increased pcharacter of $\sigma(N_{17}-H_{20})$ ie. 2.72 %. When the percentage p contribution of LP₁(O₂₇) is 42.79% while that of LP₂(O₂₇) is 99.62 %. ie. LP₂(O₂₇) is comparable to a pure π type lone pair orbital participating in electron donation to the $\sigma^*(N_{17}-H_{20})$ orbital for the interaction LP₂(O₂₇) $\rightarrow \sigma^*(N_{17}-H_{20})$ H₂₀). The low ED value of σ^* (N-H) can be due to the electron density redistribution effect which is significant for N-H^{...}O bonds [26]. The electron density 0.03039 e of $\sigma^*(N_{17}-H_{20})$ leads to a moderate stabilization energy 15.12 kJmol⁻¹ while E² of $\sigma^*(H_{24}-O_{25})$ for LP₁(O₂₃) $\rightarrow \sigma^*(H_{24}-O_{25})$ is 38.514 kJmol⁻¹. The variances in E² energies are due to accumulation of electron density not only from the n(O) of hydrogen-acceptor but also from the whole molecule. The E² values of donor acceptor interaction among LP (O₂₃) and LP (O₂₇) with $\sigma^*(H_{24}-O_{25})$ and $\sigma^*(N_{17}-H_{20})$ respectively enumerate the strength of intramolecular hydrogen bonding. Interactions between LP₂ (O₂₅) $\rightarrow \pi^*(C_{26}-O_{27})$ gives out an enormous energy due to the accumulation of charge density and intensive interaction between N-H leading to strong delocalization.

The natural hybrid orbital (NHO) directional analysis in the NBO output exhibits the angular variation of NHO with the direction of line joining the two nuclear centres giving an insight about deviation (DEV) and thereby charges transfer. It also presents evidence about the direction of geometry changes followed due to optimization of the molecular structure. For NHOs in σ bonding orientation, DEV values are ~ 0°, whereas perpendicular π type orientation corresponds to DEV = ~90° [23]. The DEV tabulated in Table 4 gives bending angles of most significant bonds. The existence of deviation for all the ring atoms represents the conjugative effect and increase of strains at the active centre of the compound [27]. Among the ring carbon atoms, C₄ shows highest DEV due to substitution effect [28-29]. Similarly, a remarkable deviation of 2.9° is obtained for C₁₅ atom participating σ (C₁₂-C₁₅) due to the presence of zwitterionic groups NH₃⁺ and COO. The extent of resonance interaction is high when O₂₃ is in the same plane with fumaric acid moiety. Due to strong O₂₅-H₂₄⁻⁻⁻O₂₃ intramolecular hydrogen bonding interaction of stabilization energy 38.514 kJmol⁻¹, O₂₃ is twisted away from the line of center of σ (C₂₁-O₂₃) by angle 2.9°. O₂₅ and C₂₆ shows a markable deviation of 5.1° and 4.0° from the line of center of

bonds σ (H₂₄–O₂₅) and σ (O₂₅–C₂₆) respectively whereas the NHO of H₂₄ goes in line with σ (H₂₄–O₂₅) axis and DEV value comes under the threshold printing limit of 1.0°. The alignment of H₂₄ atom is not deviated from σ (H₂₄-O₂₅) bond axis since it lies in the strong charge transfer path.

- Position for Table 2
- Position for Table 3
- Position for Table 4

4.3 Vibrational spectral analysis

The vibrational spectral analysis is completed on the basis of the characteristic vibrations of the substituted pyridine. The experimental FT-IR, FT- Raman spectra and B3LYP/6-31G(d) level simulated theoretical spectra are shown in Figs. 4 and 5. The detailed analyses of vibrational wavenumbers and the confirmation of the presence of various functional groups (Table 5) are discussed below. The wavenumber discrepancies of simulated and experimental spectra are owing to the dissimilar circumstances in which they are obtained. Theoretical spectrum is achieved from an isolated optimized molecule in gas phase and experimental spectra is measured in solid phase, which may get influenced by inter and intramolecular interactions.

- Position for Table 5
- Position for Figure 4
- Position for Figure 5

4.3.1 Phenyl ring vibrations

Normal mode vibrations of monosubstituted benzene ring is studied and assigned with Wilson's numbering system [30]. Monosubstituted benzene has five C-H stretching modes 2, 7a,

7b, 20a, and 20b out of which only 20a, 20b, 2 and mode 7a are active in the IR spectrum. A very strong band at 3061 cm⁻¹ in Raman spectra is assigned as mode 20a while a strong peak at 3029 cm⁻¹ in the IR spectra corresponds to mode 20b. The band found at 3041 cm⁻¹ in Raman is identified as mode 2. The strong band in IR at 3000 cm⁻¹ and medium band at 3008 cm⁻¹ in Raman is assigned to mode 7a of the phenyl ring. The intensity of the C-H ring stretching is reduced and multiple weak bands are observed in IR around 3029 cm⁻¹ because NH₃⁺ and CH₂ group stretching vibrations fall in the same region [31]. Two doubly degenerate C-C stretching of the benzene ring is attributed to mode e_{2g} and e_{1u} . The mode 8a appears as strong peaks at 1591 cm⁻¹ and 1601 cm⁻¹ in IR and Raman respectively, while 8b is found at a lower wavenumber 1586 cm⁻¹ as a medium intensity peak in Raman. Mode 19a is assigned to weak band at 1491cm⁻¹ in Raman and a strong peak at 1490 cm⁻¹ in IR whereas mode 19b is identified at 1446 cm⁻¹ in IR as weak band and at 1445 cm⁻¹ in Raman spectra as medium peak. Normal mode 14 is found as a medium band at 1304 cm⁻¹ in IR and a weak band at 1312 cm⁻¹ in Raman. Among the C-C aromatic stretching modes 8a, 19a and 14 are simultaneously active in both IR and Raman measurements which is an indication of charge transfer interaction. Modes 8a and 19a are coupled with C-H bending motion of the phenyl ring to a greater extend which is clearly depicted in Table 5.

The C-H in plane bending vibrations are assigned to modes 3, 9a, 15, 18a and 18b. The bands at 1339 cm⁻¹ and 1341 cm⁻¹ in both IR and Raman respectively correspond to mode 3. The weak band at 1165 cm⁻¹ in IR corresponds to mode 9a and a medium band at 1160 cm⁻¹ in Raman denotes mode 15. The medium peak at 1075 in IR refers to mode 18b. Radial skeletal vibrations of monosubstituted benzene is denoted by 1, 12, 6a and 6b in Wilson's numbering system [30]. The frequency of 6a is highly variable from 300 cm⁻¹ to 530 cm⁻¹ while that of 6b is identified at

a rather stable range 605-630 cm⁻¹ [30]. The weak bands found in the Raman spectra at 315 cm⁻¹ and 620 cm⁻¹ are identified as 6a and 6b modes respectively. A strong polarized peak around 1000 cm⁻¹ is expected in Raman for mode 12 [30]. The strong band appearing in Raman at 1002 cm⁻¹ is assigned for mode 12. Other radial deformations, out of plane CH bending and skeletal vibrations are indicated in Table 5.

4.3.2 CH₂ Vibrations

The CH₂ antisymmetric stretching is expected around 2926 cm⁻¹ in IR and Raman [32]. The strong band observed at 2949 cm⁻¹ in IR and a strong band at 2948 cm⁻¹ in Raman is attributed to asymmetric CH₂ stretching. The shifting of stretching vibration to a longer wavenumber side is due to the strain on the phenyl ring. The CH₂ wagging mode is at 1270 cm⁻¹ and 1275 cm⁻¹ in IR and Raman respectively which is well inside the range of 1400–900 cm⁻¹ [32, 33].

4.3.3 Carbonyl vibrations

Amino acids in the zwitterionic form having deprotonated carboxyl group COO⁻ gives two significant characteristic bands, due to asymmetric and symmetric stretching. Asymmetric stretching falls in the region 1605-1585 cm⁻¹ whereas symmetric stretching is expected within 1425-1393 cm⁻¹ [34-35]. The medium IR band present at 1695 cm⁻¹ and a strong Raman equivalent at 1690 cm⁻¹ is assigned for asymmetric stretching of COO⁻. The blueshifting is due to the intramolecular O-H⁻⁻O hydrogen bonding, thereby increasing the force constant of the bond. Symmetric COO⁻ stretching is observed as medium bands in Raman at 1210 cm⁻¹. The wavenumbers corresponding to this mode is found to be significantly lowered owing to the decrease in double bond character of CO group. The lowering of the COO⁻ symmetric stretching

wavenumber is an indication of hydrogen bond formed in O_{25} - H_{24} ... O_{23} since hydrogen bonding to COO⁻ can decrease the wavenumber upto 60 cm⁻¹ [35].

4.3.4 NH₃⁺ Vibrations

N-H stretching falls in the region 3500 to 3200 cm⁻¹ [34]. The position of absorption is sensitive to the degree of hydrogen bonding and protonation results in broadening and weakening of the peaks. The expected range of asymmetric stretching after protonation is amid 3300-3100 cm⁻¹ [34,36]. The broad very strong band at 3079 cm⁻¹ in IR is assigned to NH₃⁺ asymmetric stretching. Lowering of asymmetric stretching wavenumber is due to N-H^{...}O hydrogen bond formation. For amino acids with NH₃⁺ group, the symmetric stretching come in between 3100-2800 cm⁻¹ [35]. The strong Raman band formed at 2977 cm⁻¹ is assigned for symmetric stretching of NH₃⁺ which confirms the formation of zwitterionic state [37,38].

The strong band at 1612 cm⁻¹ in IR corresponds to NH_3^+ asymmetric deformation which comes in its normal range 1615-1580 cm⁻¹ [7]. A medium band expected within the range 1550-1500 cm⁻¹ for symmetric deformation is found slightly blueshifted as a strong band at 1567 cm⁻¹ in the IR spectrum. The rocking mode of NH_3^+ is heavily coupled with stretching and bending vibrations of C_{26} - O_{25} which is mentioned in Table 5. Simultaneous presence of a medium band in IR and a very weak band in Raman at 481cm⁻¹ is due to C_{21} - C_{15} - N_{17} .

4.3.5 C-C, C-H, and C-N vibrations

C-H stretching vibrations in Raman spectrum is expected near 3000 cm⁻¹ [32]. The strong band at 2926 cm⁻¹ in Raman is identified as C-H stretching vibration. The characteristic C-N stretching vibration of the C-NH₃⁺ is found around 1000 cm⁻¹ [39]. This range comes well with in stretching vibrations of C-C [39]. The medium intensity band present at 994 cm⁻¹ in IR is assigned for C-N stretching coupled with C-C stretching. The CCH bending of fumaric acid moiety is identified as strong band in IR at 1256 cm⁻¹ while that of phenylalanine moiety is found at 1210 cm⁻¹ as a medium band in Raman due to its coupling with COO⁻ stretching vibration. CH deformation of zwitterionic amino acid falls in the range 1340-1315 cm⁻¹ [32]. The weak peak at 1370 cm⁻¹ in IR and a medium peak at 1368 cm⁻¹ in Raman is due to deformation involving C₁₅ and H₁₆.

4.3.6 Carboxylic acid vibrations

Isomeric unsaturated dicarboxylic acids exhibit very broad band in the region 3400-3600 cm⁻¹ for O-H stretching vibration [32]. The broad band in IR at 3416 cm⁻¹ corresponds to O-H stretching of carboxylic group in the fumaric acid moeity. The normal range of C=O in carboxylic acid is 1725-1700 cm⁻¹, while intramolecularly hydrogen bonded acids lower the frequency range to 1680-1650 cm⁻¹ [32]. The strong peaks at 1712 cm⁻¹ in IR and at 1706 cm⁻¹ in Raman corresponds to C_{32} =O₃₃ stretching which agrees well with the normal range. The stretching of C_{26} =O₂₇ gives a downshifted strong band in IR at 1631 cm⁻¹ and medium band in Raman at 1641 cm⁻¹. The redshifting is due to its strong coupling with NH₃⁺ bending vibrations indicating the formation of strong intramolecular hydrogen bond between N₁₇-H₂₀···O₂₇. The hyperconjugative interaction between LP(1) O₂₇ and LP(2) O₂₇ with $\sigma^*(N_{17}$ -H₂₀) resulting in a high stabilization energy value of 15.12 and 20.41 kJmol⁻¹ respectively shows the presence of intramolecular charge delocalization and thereby hydrogen bond formation. The strong peak at 1408 cm⁻¹ in IR and a weak peak at 1411 cm⁻¹ in Raman is due to interacting C-O stretch and C-O-H in plane deformation vibration of carboxylic acid group.

4.3.7 Hydrogen bonding

The formation of hydrogen bonds in phenyl alanine compounds is important because bond formation stabilizes the protein structures through dipole interactions [40]. The presence of NH_3^+ and COO⁻ makes it a zwitterion stabilized with O-H⁻⁻O and N-H⁻⁻O intramolecular hydrogen bonds. The bond distance between O₂₅ and O₂₃ is 2.6 Å which comes in the range of strong hydrogen bonds (2.4 – 2.7 Å) [41]. The band at 120 cm⁻¹ in Raman is assigned to the torsional vibration of C₂₁-O₂₃⁻⁻H₂₄-O₂₅ and a very strong peak observed at 72 cm⁻¹ is assigned for bending of O₂₅-H₂₄⁻⁻O₂₃. The stretching of O₂₃⁻⁻⁻H₂₄ is found to be coupled with NH₃⁺ torsional vibration. An overview on the vibrational band assignments point out that blueshift of stretching wavenumbers and redshift of deformation modes from the free ion values are the consequences of strong O-H⁻⁻⁻O hydrogen bonding.

4.4 Absorption spectra and solvent effects

The electronic absorption wavelengths of PAF computed in the gas phase and in aqueous solvent are presented in Table 6. The solvent effect was calculated using polarizable continuum model (PCM) method at TD CAM-B3LYP/6-31G(d) level. The experimental UV-vis spectra using aqueous solvent and simulated spectra in gas phase as well as water are shown in Fig. 6.

- Position for Figure 6
- Position for Figure 7
- Position for Table 6

The electron donating highest occupied molecular orbital (HOMO) is concentrated over the substituted phenyl ring of amino acid moiety and lowest unoccupied molecular orbital (LUMO) of fumaric acid moiety receives the electron. The pictorial representation of HOMO-LUMO is presented in Fig. 7. Thus, a charge transfer interaction takes place within the compound from molecular orbitals 74 to 75 with 'A' symmetry. The electron transference from HOMO to

LUMO is depended on the energy difference between them which has significant role in electrooptic properties, reactivity and absorption in UV-visible spectra. The energy gap calculation at B3LYP/6-31G(d) level in gas phase is calculated as 3.793 eV, which is much smaller than most of the phenylalanine and fumaric acid complexes (5.405 eV for L-phenylalanine-benzoic acid, 5.983 for 4-Chloro-DL-phenylalanine, 5.532 eV for L-valinium fumarate, 5.932eV for N-acetyl-L-phenylalanine [8,38,42,43]. The formation of strong O-H^{...}O and N-H^{...}O hydrogen bond amid the charged moieties reduced the energy gap substantially with the formation of charge transfer axis [7].

The experimental absorption spectrum in water gives a strong transition at 209 nm owing to the $\pi \rightarrow \pi^*$ transition in the aromatic ring. The simulated spectrum with water solvent shows a strong transition at 234 nm with oscillator strength of 0.0102. A high transmittance percentage in the entire visible region (380 nm – 800 nm) makes PAF a promising candidate for nonlinear optical applications.

The conceptual DFT is a valuable tool to obtain quantitative information about the chemical reactivity of compounds [44, 45]. In the conceptual DFT, electronic density is the fundamental tool to describe the electronic states of atoms and molecules. A series of chemical concepts such as electronegativity, hardness is quantitatively studied by using a set of chemical reactivity indices derived from HOMO and LUMO energy [45, 46]. Chemical reactivity indices such as chemical hardness (η), chemical potential (μ), softness (S) and electrophilicity index (ω) were calculated by the following equations [47-52].

$$\eta = (I - H) / 2$$
 (2)

$$\mu = -(I + H) / 2 \tag{3}$$

$$\mathbf{S} = 1/(\eta) \tag{4}$$

$$\omega = \mu^2 / 2\eta \tag{5}$$

where I and H are ionization potential (I = $-E_{HOMO}$) and electron affinity (H = $-E_{LUMO}$) of a molecular system. Electron affinity denotes the capacity to receive just one electron from a donor. Nevertheless, in several types of bonding like covalent hydrogen bonding, fractional charge transmission occurs within the system. Calculated value of global reactivity coefficients of PAF are presented in Table 7. The negative value of chemical potential (-7.73 eV) indicates that the compound is stable while the low magnitude of chemical hardness (1.90 eV) suggests charge transfer interaction [53, 54].

4.5 Mulliken atomic charge and molecular electrostatic potential (MEP) Analysis

Dipole moment, polarizability and electronic structure of a molecular system are influenced by the atomic charge distribution. The Mulliken atomic charges calculated at B3LYP/6-31G(d) level using Gaussian '09 is shown in Fig. 8. Among the hydrogen atoms and oxygen atoms present in PAF, H_{24} and O_{23} , which are involved in hydrogen bonding interaction possess the highest positive (0.470 e) and negative (-0.651 e) atomic charge respectively. So, extensive charge delocalization is suggested by the negative value of O_{23} and positive atomic charge of H_{24} . Atomic charges corresponding to all phenyl ring carbon atoms are negative except for C₄, pointing to the fact that electronic delocalization effect is additionally strong among carbon atoms leading to charge transfer between substituents. C₂₁ atom which is attached to the electron withdrawing O_{23} atom exhibits the highest positive charge in order to pull out the partial charges from the compound.

• Position for Figure 8

MEP mapping allows visual comparison of electrostatic potentials of each atom in a molecular system by providing different colors like red, orange, green, blue in the decreasing order of potential. MEP surface analysis allows recognizing the reactive sites for electrophilic as well as nucleophilic attack in hydrogen bonded interactions. The MEP surface plotted by mapping the electrostatic potential onto the isosurface range of -0.08847 to +0.08847 showing the relative polarity of LPF molecule obtained at B3LYP/6-31G(d) level is given in Fig. 9. The MEP map suggests electron density is mainly concentrated over lone pair of electronegative oxygen atom making it the most reactive part of the molecule while highest positive potential is found around nucleophilic H atoms in NH_3^+ group. These electrophilic and nucleophilic sites thus give a pictorial representation of regions from where the compound can have intra molecular interactions and confirm the existence of N-H⁻⁻⁻O bond formation.

• Position for Figure 9

5. Conclusion

The experimentally synthesized PAF crystals were analyzed for elaborate vibrational spectral investigation by FT-IR, FT-Raman and UV-visible studies. Molecular structure optimization and harmonic vibrational frequencies are obtained using density functional theory at B3LYP/6-31G(d) level. Existence of O-H^{\cdots}O and N-H^{\cdots}O hydrogen bond leading to the charge transfer interaction responsible for the nonlinear optical activity is studied by NBO analysis. Down shift of NH₃⁺ stretching wavenumber and upshift of NH₃⁺ deformation indicates the presence of N-H^{\cdots}O hydrogen bonding. The appearance of normal mode 8a, 19a and 14 of the phenyl ring simultaneously in FT-IR and FT-Raman spectra is an evidence for charge transfer between phenylalanine and the dicarboxylic acid moieties. Mapping of molecular electrostatic potential suggests oxygen in COO⁻ group as strong electrophilic site and hydrogen in NH₃⁺ as nucleophilic

site from where PAF can form intramolecular hydrogen bond. The low HOMO-LUMO energy gap and transparency to the entire visible region suggests PAF a potential candidate for NLO application.

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Figure captions

Fig. 1 Powder X-ray diffraction pattern of PAF

Fig. 2 Variation of SHG in PAF for the particle size 150<r<180 µm as compared to KDP

Fig. 3 Optimized structure of PAF calculated at B3LYP/6-31G(d)

Fig. 4 (a). The FT-IR spectrum of PAF molecule in the wavenumber range 4000-400 cm⁻¹ (b). The simulated infrared spectrum of PAF molecule computed at B3LYP/6-31G(d) basis set.

Fig. 5 (a). The FT-Raman spectrum of PAF molecule in the wavenumber range 4000-50 cm⁻¹. (b). The simulated Raman spectrum of PAF molecule computed at B3LYP/6-31G(d) basis set.

Fig. 6 (a) Experimental UV-Vis spectrum of PAF molecule in water solvent

(b) Simulated UV-vis spectrum in water for PAF molecule calculated with the PCM CAM-B3LYP/6-31G(d) method

(c) Simulated UV-vis spectrum of PAF molecule in the gas phase

Fig. 7 (a) HOMO plot of PAF at B3LYP/6-31G(d) (b) LUMO plot of PAF at B3LYP/6-31G(d)

Fig. 8 Mulliken charge distribution chart of PAF molecule

Fig. 9 Molecular electrostatic potential map of PAF molecule calculated at B3LYP/6-31G(d)

Table	1.	Optimized	geometrical	parameters	of PA	F by	B3LYP	/6-31G(d)	in	comparison	with
XRD	dat	a.									

Bond length (Å)		Å)	Bond	angle (°))	Dihedra	Dihedral angle (°)			
Parameter	Cal	Exp ^a	Parameter	Cal	Exp ^a	Parameter	Cal	Exp ^a		
C_1 - C_2	1.39	1.39	$C_1 - C_2 - C_3$	119.91	120.23	$C_1 - C_2 - C_3 - C_4$	-0.15	-1.13		
C_2-C_3	1.40	1.38	$C_2 - C_3 - C_4$	120.97	121.07	$C_2-C_3-C_4-C_5$	0.26	0.83		
C_3-C_4	1.40	1.39	$C_3 - C_4 - C_5$	118.66	117.91	$C_3-C_4-C_5-C_6$	-0.16	0.27		
C_4-C_5	C_4-C_5 1.40 1.3		$C_4 - C_5 - C_6$	120.39	120.84	120.84 $C_5-C_6-C_1-H_7$		-179.19		
C_5-C_6	1.39	1.38	$C_{6}-C_{1}-H_{7}$	C ₆ -C ₁ -H ₇ 120.22		$H_7-C_1-C_2-H_8$	-0.12	0.29		
C_1 - H_7	1.09	0.93	C_1 - C_2 - H_8	120.22	119.89	C_1 - C_2 - C_3 - H_9	178.74	178.90		
C_2 - H_8	1.09	0.93	$C_2-C_3-H_9$	119.45	119.45	$C_3-C_4-C_5-H_{10}$	-179.97	-179.77		
C ₃ -H ₉	1.09	0.93	$C_4-C_5-H_{10}$	119.16	119.52	$C_4-C_5-C_6-H_{11}$	179.61	178.89		
C ₅ -H ₁₀	1.09	0.93	$C_5-C_6-H_{11}$	119.53	119.60	$C_2-C_3-C_4-C_{12}$	-179.68	-179.29		
$C_{6}-H_{11}$	1.09	0.93	$C_5 - C_4 - C_{12}$	121.01	120.86	$C_5 - C_4 - C_{12} - H_{13}$	159.27	141.40		
C_4-C_{12}	1.52	1.51	C_4 - C_{12} - H_{13}	109.48	108.56	$C_3-C_4-C_{12}-H_{14}$	-138.6	-155.04		
C_{12} - H_{13}	1.10	0.97	C_4 - C_{12} - H_{14}	110.4	108.52	$C_3 - C_4 - C_{12} - C_{15}$	103.15	83.23		
C_{12} - H_{14}	1.09	0.97	$C_4 - C_{12} - C_{15}$	115.37	114.91	C_4 - C_{12} - C_{15} - H_{16}	-170	172.19		
$C_{12}-C_{15}$	1.53	1.54	C_{12} - C_{15} - H_{16}	109.36	107.83	$C_4 - C_{12} - C_{15} - N_{17}$	-51.65	-69.39		
$C_{15}-H_{16}$	1.10	0.98	C_{12} - C_{15} - N_{17}	113.78	111.96	C_{12} - C_{15} - N_{17} - H_{18}	-74.75	-56.04		
C ₁₅ -N ₁₇	1.51	1.49	C ₁₅ -N ₁₇ -H ₁₈	115.47	109.47	C_{12} - C_{15} - N_{17} - H_{19}	161.2	-176.04		
$H_{18}-N_{17}$	1.02	0.89	C_{15} - N_{17} - H_{19}	101.55	109.48	C_{12} - C_{15} - N_{17} - H_{20}	53.64	64.01		
$H_{19}-N_{17}$	1.05	0.89	C_{15} - N_{17} - H_{20}	111.89	109.47	C_4 - C_{12} - C_{15} - C_{21}	68.58	54.30		
$H_{20}-N_{17}$	1.04	0.89	C_{12} - C_{15} - C_{21}	115.24	111.08	H_{16} - C_{15} - C_{21} - O_{22}	-84.97	-46.70		
$C_{15}-C_{21}$	1.58	1.52	$C_{15}-C_{21}-O_{22}$	117.45	117.97	N_{17} - C_{15} - C_{21} - O_{23}	-18.35	17.80		
C_{21} - O_{22}	1.23	1.25	$C_{15}-C_{21}-O_{23}$	112.15	115.22	$C_{15}-C_{21}-O_{23}-H_{24}$	105.09	89.31		
$C_{21}-O_{23}$	1.29	1.25	$C_{21}-O_{23}$ H_{24}	115.62	129.89	$C_{21}-O_{23}$ $H_{24}-O_{25}$	-91.12	-105.16		
O_{23} H_{24}	1.58	1.83	$O_{22}-C_{21}-O_{23}$	130.39	124.56	O_{23} H ₂₄ -O ₂₅ -C ₂₆	15.08	10.47		
$H_{24}-O_{25}$	1.02	0.82	O_{23} H ₂₄ -O ₂₅	175.76	168.16	$H_{24}-O_{25}-C_{26}-O_{27}$	-1.17	5.75		
$O_{25}-C_{26}$	1.32	1.32	$H_{24}-O_{25}-C_{26}$	112.55	109.46	$H_{24}-O_{25}-C_{26}-C_{28}$	179.1	-174.76		
$C_{26}-O_{27}$	1.23	1.21	$O_{25}-C_{26}-O_{27}$	126.23	123.65	O_{27} - C_{26} - C_{28} - H_{29}	-177.17	-172.75		
$C_{26}-C_{28}$	1.49	1.48	O_{25} - C_{26} - C_{28}	111.81	112.71	O_{25} - C_{26} - C_{28} - C_{30}	-176.93	-172.24		
$C_{28}-H_{29}$	1.08	0.93	C ₂₆ -C ₂₈ -H ₂₉	117.08	119.92	C_{26} - C_{28} - C_{30} - H_{31}	0.06	2.29		
$C_{28}-C_{30}$	1.34	1.32	C_{26} - C_{28} - C_{30}	120.89	120.09	C_{26} - C_{28} - C_{30} - C_{32}	179.57	-177.70		
C ₃₀ -H ₃₁	1.09	0.93	C ₂₈ -C ₃₀ -H ₃₁	120.41	118.36	C ₂₈ -C ₃₀ -C ₃₂ -O ₃₃	-179.05	169.16		
C_{30} - C_{32}	1.48	1.49	C_{28} - C_{30} - C_{32}	124.53	123.30	C ₂₈ -C ₃₀ -C ₃₂ -O ₃₄	0.92	-11.15		
C ₃₂ -O ₃₃	1.21	1.20	C_{30} - C_{32} - O_{33}	123.69	121.66	C ₃₀ -C ₃₂ -O ₃₄ -H ₃₅	-179.91	168.16		
O ₃₄ -C ₃₂	1.36	1.31	C ₃₀ -C ₃₂ -O ₃₄	113.6	113.05					
H ₃₅ -O ₃₄	0.98	0.82	C ₃₂ -O ₃₄ -H ₃₅	105.92	109.44					
H_{20} O_{27}	1.81	2.05								
O ₂₃ H ₁₉	1.84	2.18								

^aTaken from Ref [15]

Table 2. NBO results showing the formation of Lewis and Non-Lewis orbitals by the valence hybrids corresponding to the intramolecular N-H^{...}O hydrogen bonds of PAF

BOND (A- B)	ED (e)	Energy (kJmol ⁻¹)	ED _A (%)	$ED_B(\%)$	NBO	S (%)	P (%)
σ*(H ₂₄ -O ₂₅)	0.03149	2148.302	75.33	24.67	0.8679 (s) _H -0.4967 (sp ^{1.95}) _O	100.00 33.84	- 66.08
$\sigma^*(C_{21}-O_{23})$	0.05995	1605.266	66.33	33.67	$0.8144 (sp^{2.04})_{C}$ -0.5803(sp^{1.44})_{C}	32.86 40.87	67.02 58.83
$\sigma^*(O_{25}-C_{26})$	0.08052	1050.270	32.54	67.46	$0.5705(sp^{2.03})_{0}$ -0.8213(sp^{2.44})_{0}	32.93	67.00 70.75
$\sigma(C_{21}-O_{23})$	1.99683	-2524.340	33.67	66.33	$0.5803(\text{sp}^{-0.04})_{\text{C}}$	32.86	67.02
$LP_1(O_{23})$	1.96023	-1633.294	-	-	$+0.8144 (sp)_{0.69} (sp)_{0.$	40.87 58.98	40.99
$LP_1(O_{25})$ $LP_1(O_{27})$	1.96843 1.96963	-1405.482 -1825.304	-	-	sp sp ^{0.75}	33.07 57.16	66.83 42.79
$LP_2(O_{23})$ $LP_2(O_{27})$	1.87653 1.86146	-529.672 -736.32	-	-	sp ^{99.99} sp ^{99.99}	0.13 0.17	99.70 99.62
$\sigma(N_{17}-H_{18})$	1.99274	-2121.574	69.84	30.16	0. 5492 (sp ^{3.29}) _N -0. 8357 (s) _H	23.30 100	76.64 -
$\sigma(N_{17}-H_{19})$	1.99147	-2107.56	70.80	29.20	$0.8415(sp^{3.14})_{N}$ +0.5403(s) _H	24.16 100	75.79 -
σ(N ₁₇ -H ₂₀)	1.99092	-2106.754	72.79	27.21	$0.8531(\text{sp}^{2.72})_{\text{N}}$ +0.5217 (s) ₁₄	26.85 100	73.11
σ* (N ₁₇ -H ₁₈)	0.01085	1545.96	30.16	69.84	$0.5492 (\text{sp}^{3.29})_{\text{N}}$	23.30 100	76.64
σ* (N ₁₇ -H ₁₉)	0.00801	1590.446	29.20	70.80	$0.5403 (\text{sp}^{3.14})_{\text{N}}$	24.16	75.79
σ* (N ₁₇ -H ₂₀)	0.03039	1702.948	27.21	72.79	$0.5217 (\text{sp}^{2.72})_{\text{N}}$	26.85	73.11
					0.0331 (3)H	100	

Donor (i)	ED(<i>i</i>) (e)	Acceptor (j)	ED(<i>j</i>) (e)	$E^{(2)a}$ (kJmol ⁻¹)	$\frac{E(j) - E(i)^{b}}{(arb. units)}$	$F(I, j)^{c}(arb. units)$
π(C ₂ C ₃)	1.68821	$\pi^{*}(C_{1}-C_{6})$ $\pi^{*}(C_{4}-C_{5})$	0.31273 0.33411	78.162 84.63	0.30 0.30	0.067 0.070
$\pi(C_4-C_5)$	1.65703	$\pi^*(C_1-C_6)$ $\pi^*(C_2-C_3)$	0.31273 0.33444	84.378 89.586	0.29 0.28	0.069 0.069
$\pi(C_1 - C_6)$	1.66722	$\pi^*(C_2 - C_3)$ $\pi^*(C_4 - C_5)$	0.33444 0.33411	89.796 85.47	0.29 0.29	0.070 0.069
n ₂ (O ₂₂)	1.86585	$\begin{array}{l} \sigma^{*}(C_{15}\text{-}C_{21}) \\ \sigma^{*}(C_{21}\text{-}O_{23}) \end{array}$	0.11178 0.05995	90.888 92.148	0.57 0.79	0.099 0.120
From unit 1	to unit 2					
n ₁ (O ₂₃)	1.96023	$\sigma^*(H_{24}-O_{25})$	0.03149	38.514	1.45	0.103
From unit 2	to unit 1					
n ₁ (O ₂₇)	1.96963	$\sigma^*(N_{17}-H_{20})$	0.03039	15.12	1.36	0.062
n ₂ (O ₂₇)	1.86146	$\sigma^*(N_{17}-H_{20})$	0.03039	20.412	0.94	0.062
Within unit	2					
n ₂ (O ₂₅)	1.76508	<i>π</i> *(C ₂₆ –O ₂₇)	0.29420	248.598	0.32	0.125
n ₂ (O ₃₄)	1.81836	π*(C ₃₂ –O ₃₃)	0.24092	212.478	0.37	0.123

Table 3. Second-order perturbation theory analysis of Fock matrix in NBO basis

Bond (A-B)	Deviation at A (°)	Deviation at B (°)
σ(C ₁ -C ₂)	2.6	2.2
$\sigma(C_1-C_2)$	2.3	1.9
σ(C ₂ -C ₃)	1.8	1.8
$\sigma(C_3-C_4)$	1.3	2.7
$\sigma(C_4-C_5)$	3.0	1.3
$\sigma (C_{12} - C_{15})$	1.6	2.9
σ(C ₂₆ -O ₂₇)	4.2	4
$\pi(C_{26}-O_{27})$	87.3	87.5
σ(C ₃₂ -O ₃₃)	4.6	3.8
π (C ₃₂ -O ₃₃)	87.7	87.7
σ(C ₂₁ -O ₂₂)	5.3	4.6
π (C ₂₁ -O ₂₂)	86.6	87.6
σ (C ₂₁ –O ₂₃)	3.2	2.9
σ (H ₂₄ -O ₂₅)		5.1
σ (O ₂₅ -C ₂₆)	3.9	4.0

Table 4. NHO directionality and "bond bending" (deviations from line of nuclear centers)

5-C26)

(cm^{-1})	Scaled v_i	(cm^{-1})	v_{Raman} (cm ⁻¹)	IR int ^a	Raman act ^b	Force constants	Assignments with PED (%) ^c
3701	3560	3416 br	-	0.35	3.48	8.5874	vO ₃₄ H ₃₅ (100)
3515	3378	3079 vs	-	0.62	2.92	7.8733	NH ₃ ⁺ as (93)
3238	3110	-	3061vs	4.6	0.33	6.7152	^{20a} vCHar (96)
3234	3109	-	-	1.59	2.62	6.7568	vCH (95)
3218	3094	-	-	2.57	3.72	6.681	vCH (83)
3208	3084	-	-	1.25	4.51	6.645	vCHar (88)
3196	3072	-	3041sh	2.68	2.58	6.5672	2 vCHar (90)
3186	3062	3029 s	-	6.32	2.49	6.496	^{20b} vCHar (86)
3167	3045	-	-	11.93	4.65	6.2906	NH ₃ ⁺ ips (89)
3162	3041	3000 s	3008 m	1.19	1.74	6.4123	^{7a} vCHar (75), NH ₃ ⁺ ips (14)
3159	3037	-	2977s	1.57	0.89	6.2975	NH ₃ ⁺ ips (82), vCHar (10)
3115	2994	2949 s	2948 s	11.77	2.43	6.2624	CH ₂ as (90)
3081	2963		2926 s	2.41	8.11	6.0713	vC ₁₅ H ₁₆ (88), CH ₂ ss (11)
3047	2929	\mathbf{Q}^{\prime}	2863 m	2.13	2.77	5.845	CH ₂ ss (79), vC ₁₅ H ₁₆ (11), CH ₂ as (10)
2817	2712	-	-	16.64	13.54	5.0706	$vO_{25}H_{24}$ (89)
1827	1760	1712 s	1706 s	20.36	17.46	17.8781	vC ₃₂ =O ₃₃ (78)
1798	1726	1695 m	1690 s	43.86	0.39	18.6142	COO ⁻ as (78)
1762	1694	1631s	1641m	7.06	1.65	5.6138	vO ₂₆ =C ₂₇ (51), NH ₃ ⁺ opb (19)
1718	1651	-	-	2.12	18.36	9.2503	$\nu C_{28}C_{30}$ (64), $\delta H_{29}C_{28}C_{30}$ (10)
	·	•				•	•

Table 5. Vibrational assignment of PAF by normal mode analysis based on Scaled Quantum Mechanical force field calculations

		l	ACCEPT	ED MAN	USCRIP	Т	
1687	1622	1612 s	-	28.18	10.78	2.4339	NH ₃ ⁺ opb (50), vO ₂₆ =C ₂₇ (21)
1665	1600	1591s	1601s	1.76	3.43	8.8635	^{8a} vCCar (51), Rtrigd (17), δCHar (14)
1642	1579	-	1586 m	41.21	1.15	8.4902	^{8b} vCCar (67)
1634	1571	1567 s	-	25.9	1.95	1.6894	NH ₃ ⁺ ipb (65), CNH ₃ t (20), NH ₃ rk (11)
1546	1486	1490 s	1491 w	4.35	0.17	3.072	δCHar (60), ^{19a} δCCar (12)
1509	1449	-	-	18.81	2.69	1.5088	CH ₂ sci (77)
1503	1445	1446 w	1445 m	49.07	0.19	2.8213	δCHar (47), ^{19b} νCCar (24)
1476	1423	-	-	33.09	1.08	1.8636	NH ₃ ⁺ rk (38), νO ₂₅ C ₂₆ (12), δC ₂₆ Oh (11)
1459	1403	1408 s	1411 vw	56.85	0.62	2.1031	$vO_{25}C_{26}$ (24), NH ₃ ⁺ rk (22), $\delta C_{26}Oh$ (18)
1401	1345	1370 w	1368 m	34.98	3.05	1.5958	$τH_{16}C_{15}C_{21}$ (32), CH ₂ wag (23), $\delta H_{16}C_{15}C_{21}$ (14)
1396	1342	-		6.1	1.62	3.236	$vC_{30}C_{32}$ (35), $\delta C_{32}Oh$ (30), $\delta O_{33}C_{32}O_{34}$ (18)
1390	1336			0.67	0.66	1.5785	$\begin{aligned} \tau H_{16}C_{15}C_{21} \ (26), \delta \\ H_{16}C_{15}C_{21} \ (14), \\ \delta CHar \ (11) \end{aligned}$
1372	1319	1339 w	1341 m	37.59	0.34	1.7033	³ δCHar (64)
1355	1303	1304 m	1312 w	12.21	1.08	3.0911	14 vCCar (43)
1336	1284	_	-	28.82	3.17	1.7554	$\begin{array}{l} \delta C_{26} Oh \ (22), \\ \delta H_{29} C_{28} C_{30} \ (13), \\ \nu O_{25} C_{26} \ (12) \end{array}$
1325	1274	1270 m	1275 m	26.99	2.89	2.1202	CH ₂ wag (18), vC ₁₂ C ₁₅ (10)
1311	1258	1256 s	-	8.04	4.91	1.6616	$\delta H_{29}C_{28}C_{30}$ (44)
1298	1250	-	1210 m	37.52	0.72	3.2016	COO ⁻ ss (47), $\delta H_{16}C_{15}C_{21}$ (11)

		A	ACCEPT	ED MAN	USCRIP	Т	
1247	1198	-	-	26.52	0.13	1.4386	$\begin{array}{l} \delta H_{29}C_{28}C_{30}\ (50),\\ \nu O_{25}C_{26}\ (16) \end{array}$
1235	1188	1187 s	1185 m	23.97	2.56	1.513	δCH ₂ (31), νC ₄ C ₁₂ (22)
1226	1178	-	-	1.45	2.08	1.4106	δCH ₂ (17), CH ₂ wag(18), νC ₄ C ₁₂ (11), δCHar(10)
1218	1171	1165 w	-	8.59	1.83	1.0366	^{9a} δCHar(62), vCCar (23)
1200	1155	-	-	6.57	6.3	1.4889	$\begin{array}{l} \delta C_{32} Oh(45), \nu C_{30} C_{32} \\ (22), \delta H_{29} C_{28} C_{30} \left(15\right) \end{array}$
1194	1148	-	1160 m	0.53	1.03	0.9276	¹⁵ δCHar(73)
1142	1098	-	-	5.53	1.37	1.0909	CNH ₃ t (25), δH ₁₆ C ₁₅ C ₂₁ (24)
1118	1074	1075 m	-	35.05	0.74	1.2131	vCCar (30), ^{18b} δCHar (25)
1104	1062	-	-	13.17	0.8	1.0245	CNH ₃ t (30), vCCar (11), τH ₁₆ C ₁₅ C ₂₁ (10)
1076	1033	1029 w	1031 m	2.32	0.3	0.7576	$\begin{aligned} \tau C_{21} O_{23} & \stackrel{\dots}{} H_{24} O_{25} (45), \\ \tau C_{28} COH_{24} (26) \end{aligned}$
1060	1019	-	1002 s	3.51	3.36	1.4616	vCCar (46), ¹² Rtrgd (22)
1037	997	994 m		0.5	1.23	1.2704	νC ₁₂ C ₁₅ (21), νCN (17)
1036	995		-	39.35	0.19	0.6961	τC ₃₀ H (89)
1018	981	\mathbf{O}	-	7.72	6.89	3.5576	δCCar (52), vCCar (36)
1005	966	960 m	963 w	2.54	0.21	0.7544	⁵ τCHar (73)
978	940	-	-	82.98	0.16	0.762	^{17a} τCHar (68), τCCar (19)
974	937	-	-	7.82	1.2	2.0993	$vC_{26}C_{28}$ (53), $\delta C_{30}C_{28}C$ (10)
959	922	917 s	-	9.69	1.9	1.0464	vC ₁₂ C ₁₅ (15), CH ₂ wag (22)
935	899	897 s	901 w	58.64	0.76	0.7264	^{10b} τCHar (72)

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923	886	-	-	0.35	5.2	1.188	τC ₂₈ H (65), τΟCO (19)					
919	884	-	-	271.69	1.16	2.2424	$vC_{32}O_{34}(76)$					
891	856	-	-	2.15	1.99	1.2644	νCN (20), τCOO ⁻ (12)					
869	835	850 m	857 vw	2.73	2.47	0.5591	$^{10a}\tau CHar$ (91)					
847	815	822 w	820 m	15.23	0.61	1.4786	νC ₁₅ C ₂₁ (22), δCOO ⁻ (20)					
803	772	775 m	771 w	102.34	2.53	1.3292	δCOO ⁻ (17), vCN (16), τCHar (15)					
787	757	-	-	233.44	0.03	3.1671	τCOCO (85)					
772	743	-	-	107.87	5.02	1.4141	δCCar (36), vC ₄ C ₁₂ (16), τCOO ⁻ (13), Rtrigd (10)					
755	726	744 s	745 w	8.5	0.98	0.7341	¹¹ τCHar (37), τCOO ⁻ (14)					
718	691	700 vs	697 w	130.03	0.48	0.6232	⁴ Rpuk (47), τCHar (24)					
693	667	681 sh	-	16.46	3.4	1.4337	δOC ₂₆ O (54)					
660	635	635 vs	Â	6.09	3.82	0.5781	τOC ₂₈ O (69), τC ₂₈ H (19)					
636	612	-	620 w	47.18	2.82	1.495	^{6b} Rsmd (80)					
618	595	594 m	593 vw	108.43	1.59	0.9262	$\delta C_4 C_{12}$ (14), Rasmt (13), Rpuk (11), δCOO^- (11)					
610	587	543 w	-	9.93	0.68	0.96	δO ₃₃ C ₃₂ O ₃₄ (57), δOC ₂₆ O (11)					
585	563	525 vs	-	88.88	2.06	0.3674	τC ₃₂ OOH (58)					
582	560	-	-	225.76	1.97	0.5239	τC ₃₂ OOH (31), νC ₁₅ C ₂₁ (14), δCOO ⁻ (13)					
561	540	-	-	3.37	0.39	0.9126	$\delta C_{28} C_{26} C$ (71)					
524	504	481 m	481 vw	12.4	2.33	0.8818	δCCN (46), vC ₁₅ C ₂₁ (16), vCN (11)					

		ŀ	ACCEPT	ED MAN	USCRIP	Τ	
486	467	-	462 vw	10.85	3.36	0.5843	^{16b} Rasmt (38), Rtrigd (14)
437	421	-	418 vw	79.28	1.57	0.4802	τNCC (24), ^{16a} Rasmt (18)
425	410	-	-	1.79	1.48	0.7019	δCCO (33), vC ₃₀ C ₃₂ (11)
419	403	-	-	1.58	0.16	0.3239	τCCar (72), τCHar (12)
396	381	-	-	272.71	1.72	0.2669	δC ₂₁ O ₂₃ (59)
361	348	-	315 w	31.73	1.21	0.1606	^{6a} δCCar (48)
313	302	-	-	164.95	0.75	0.3168	$δC_{28}C_{30}C$ (30), δCCO (14), $δO_{25}H_{24}$ O ₂₃ (10)
255	246	-	-	439.49	6.55	0.0678	τNH_3^+ (36), $\nu O_{23}^{}H_{24}$ (21)
245	236	-	-	252.54	8.33	0.1665	τNCC (21), τCCar (15), δC ₄ C ₁₂ (11)
221	213	-	208 m	1873.62	3.16	0.0884	$\tau N H_3^+$ (19), $\nu O_{23}^{} H_{24}$ (13)
203	196	-	-	21.85	4.61	0.1239	τCC (41), τCCar (14)
183	177	-	-	51.31	6.56	0.0956	$τC_{28}C_{30}$ (32), $τC_{28}COH_{24}$ (13)
168	162	-	-	1.28	3.59	0.0735	$τO_{23}$ H ₂₄ (30), δC ₂₈ C ₃₀ C (12)
160	154	G	-	177.46	3.91	0.0746	$ vO_{23} H_{24} (23), \delta O_{25}H_{24} O_{23} (15), \delta C_{28}C_{30}C (12) $
144	139	-	120 sh	59.64	6.1	0.0405	$\tau O_{23}^{}H_{24}$ (77)
106	102	-	101 vs	774.21	11.35	0.0465	$\tau O_{23} H_{24}(50),$ $\delta C_4 C_{12} (12)$
89	86	-	-	0.98	16.21	0.0393	$\tau O_{23}^{}H_{24}(61)$
80	78	-	72 vs	25.33	6.71	0.0262	$\delta O_{25}H_{24}$ $O_{23}(30)$
69	67	-	-	17.27	15.62	0.021	$τ C_{28}COH_{24}$ (12), δO ₂₅ H ₂₄ O ₂₃ (10),

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							$\tau C_{28}C_{30}$ (10)						
60	56	-	-	7.02	42.64	0.0126	$\begin{array}{l} \delta C_{28}C_{30}C(24),\\ \delta O_{25}H_{24} ^{}O_{23}(12),\\ \tau O_{23} ^{}H_{24}(11), \delta\\ C_4C_{12} (10), \delta C_{26}OH\\ (10) \end{array}$						
52	51	-	-	0.08	63.31	0.0095	$\tau C_4 C_{12}$ (62)						
34	33	-	-	0.04	15.91	0.0046	$\tau O_{23}^{\cdots} H_{24}(62)$						
19	19	-	-	45.98	99.63	0.0013	τCOO ⁻ (61)						
15	15	-	-	72.82	54.75	0.0011	$\begin{aligned} \tau O_{23} & {} H_{24}(30), \\ \tau C_{28} C_{30}(21), \\ \tau C_{28} COH_{24} \ (19), \\ \delta O_{25} H_{24} & {} O_{23}(14) \end{aligned}$						

br, broad; vs, very strong; s, strong; m, medium; sh, shoulder; w, weak; vw, very weak;

R / ar; Aromatic ring;v, stretching; ss, symmetric stretching; as, asymmetric stretching; ips, in plane stretching; ops, out of plane stretching; sb, symmetric bending; b/ δ , bending; ipb, in plane bending; opb, out of plane bending; t, torsion; sci, scissoring; rok, rocking; ipr, inplane rocking; opr, out of plane rocking;df, deformation; trigd, trigonal deformation; smd, symmetric deformation; asmd, asymmetric deformation; smt, symmetric torsion; ast, asymmetric torsion; puk, puckering.

- ^a Calculated IR intensities. ^b Relative Raman intensities normalized to 100 *cf.* eqn. (1).
- ^c Only PED values greater than or equal to 10% are given.

Gas phase				Water					
Excitation	Wavelength (nm)	Energy (kJmol ⁻¹)	Oscillat or strength	Excitation	Wavelo (nn Cal.	ength 1) Exp.	Energy (kJmol ⁻¹)	Oscillat or strength	
$69 \rightarrow 75$ $72 \rightarrow 75$ $74 \rightarrow 75$	280.92	11587.6	0.0006	$\begin{array}{c} 67 \rightarrow 75 \\ 67 \rightarrow 78 \\ 68 \rightarrow 75 \\ 69 \rightarrow 75 \\ 70 \rightarrow 75 \\ 74 \rightarrow 75 \end{array}$	257.23	- Q	12655.0	0.0024	
$68 \rightarrow 75$ $69 \rightarrow 75$ $73 \rightarrow 75$ $74 \rightarrow 75$	260.00	12454.3	0.0016	$\begin{array}{c} 67 \rightarrow 75 \\ 68 \rightarrow 75 \\ 69 \rightarrow 75 \\ 69 \rightarrow 78 \\ 70 \rightarrow 75 \\ 74 \rightarrow 75 \end{array}$	243.99		13341.5	0.0004	
$73 \rightarrow 76$ $73 \rightarrow 78$ $74 \rightarrow 77$	256.00	12696.4	0.0020	$\begin{array}{c} 67 \rightarrow 75 \\ 71 \rightarrow 75 \\ 72 \rightarrow 75 \\ 73 \rightarrow 75 \\ 74 \rightarrow 75 \end{array}$	234.00	209	13994.2	0.0102	

Table 6. Calculated absorptions, energy and oscillator strength of LPF using PCM method at TD CAM-B3LYP/6-31G(d) level

Parameter	Values (eV)
НОМО	-9.63
LUMO	-5.84
HOMO-LUMO Energy gap	3.79
Chemical hardness (ŋ)	1.90
Chemical potential (µ)	-7.73
Chemical softness (S)	0.53
Electrophilicity index (ω)	15.79

Table 7. Calculated HOMO-LUMO energy and global reactivity coefficients of LPF crystal



















Highlights

- FT-Raman, FT-IR and UV-Vis spectra were used to investigate *L-Phenylalanine fumaric acid* crystal.
- The vibrational analysis explicates the NLO activity and various electronic effects of the molecule supported by using density functional theory (DFT) calculations.
- The solvent effect was calculated using TD B3LYP/6-31G(d) method
- Mulliken charge analysis and molecular electrostatic potential mapping have been studied.