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A Spectroscopic Approach: Structural and Nonlinear Optical Properties of L-Prolinium Tartrate

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Abstract: In this work, the experimental and theoretical spectra of L –Prolinium Tartrate (LPT) were studied. The Fourier transform infrared of LPT was recorded in the solid phase. The optimized geometry was calculated by B3LYP method with 6-31+G (d,p) basis set. A detailed interpretation of the infrared spectrum of LPT was reported. The results were compared with the experimental values. The first hyperpolarizability values have been computed using DFTquantum mechanical calculation. The calculated results (β_0) show that the title molecule might have nonlinear optical (NLO) behavior. The HOMO-LUMO energies were also calculated.

Keywords: L-Prolinium Tartrate, Structural and Nonlinear Optical Properties, Spectroscopic Approach.

Introduction

Density functional theory is an approach for the description of ground state properties of metals, semiconductors, and insulators. The recent interest in new organic materials for photonicsaims at finding criteria for the preparation of the best materials with large nonlinear optical (NLO) response. From the microscopic viewpoint the intrinsic properties which have to beoptimized and which are essential in the comparison of different compounds are the molecular hyperpolarizabilities α, β and γ.Inthe search for new efficient organic materials to be used in nonlinearoptics for the development of molecular devices, polyenicmolecules are of particular interest[1]. Organic nonlinear optical materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultrafast response times, and high opticalthresholds for laser power as compared with inorganic materials[2]. On a molecularlevel, the parameters that can be changed are the relativeelectron affinities of the donor and acceptor groups and thelength and nature of the conjugated segment connecting thedonor to the acceptor. The donor and acceptor groups provide the ground state charge asymmetry of the molecule, which is required for second-order nonlinearity[3]. The presence of a strong dipole moment in the ground state, is an indication that the molecule hasan asymmetric charge distribution[4]. In this paper, determinationof the ground state dipole moment, excited state dipolemoment and the first hyperpolarizability of the NLO moleculeLPT are discussed in detail.

The present work deals with FTIR study of the organic NLO crystal LPT to elucidate the correlation between the molecular structure, NLO property and second order hyperpolarizability of the material supported by using potential energy distribution analysis based on density functional theory.

Materials and Methods

Synthesis

Single crystal of LPT was grown from L-Proline and L-Tartaric acid taken in the equimolar ratio were dissolved in aqueous solution by slow evaporation method. Optically clear and well-shaped crystals were obtained.

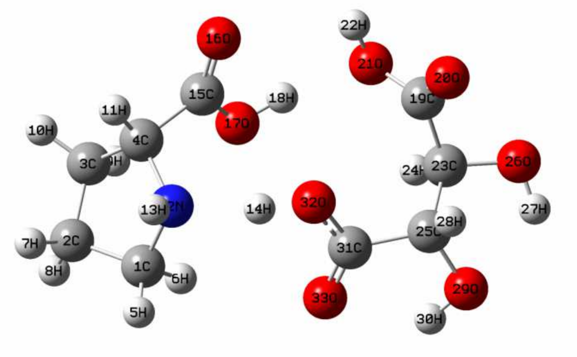


Figure 1. Structure of L Prolinium Tartrate

Characterization

The FT-IR spectra were recorded in the range 400–4000 cm^{-1} with a resolution of ±4cm^{-1} and an accuracy of ±0.01 cm^{-1} on a BRUKER IFS-66V FT-IR spectrometer. The sample was mixed with KBr and the pellet technique was adopted. The various functional groups present in the grown crystals were identified and confirmed by recording the FT-IR spectrum. The SHG efficiencies of the crystals were studied using Nd:YAG Q-switched laser.

Computational Methods

The quantum calculations were performed with Gaussian 03W program[5]usingHartree-Fock (HF), DFT and Hybrid fundamentals, supplements with different basis sets. Initial geometry of the molecules were generated from standard geometrical parameters were minimized without any constraint in the potential energy surface at Hartree-Fock level, adopting the standard basis sets. The geometries were then reoptimised at B3LYP level using basis sets. The optimized structural parameters were then used for the vibrational frequency calculations to characterize all stationary points as minima. The results of the GAUSS program[6] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy introduced by using a least-square optimization of the computed to the experimental data.

Results and Discussion

Hyperpolarizability Studies

Essentials of nonlinear optics related to β

The nonlinear response of an isolated molecule in an electric field $E_i(\omega)$ can be represented as a Taylor expansion of the total dipole moment μ_t induced by the field.

$\mu_t = \mu_0 + \alpha_{ij}E_i + \beta_{ijk}E_iE_j + \ldots$ (1)

Where α_{ij} is linear polarizability, μ_0 the permanent dipole moment and β_{ijk} are the first order hyperpolarizability tensor components.

The components of first order hyperpolarizability can be determined using the relation

$\beta = \beta iii + 1/3\Sigma\ (\beta ijj + \beta jij + \beta jji)$ (2)

Using the x,y and z components the magnitude of first order hyperpolarizability (β_{tot}) tensor can be calculated by the following equation

$\beta_{tot} = (\beta_x{}^2 + (\beta_y{}^2 + (\beta_z{}^2)^{1/2}$ (3)

The complete equation for calculating the first order hyperpolarizability from GAUSSIAN 03W output is given as follows

$\beta_{tot} = (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2$ (4)

The β components of GAUSSIAN 03W output are reported in atomic units, the calculated values have to be converted into electrostatic units (1 a.u = 8.3693 x 10^{-33}esu).

Table 1.Hyperpolarizability of LPT molecule

β_{xxx}	11.5810304
β_{xxy}	-37.7392819
β_{xyy}	14.6843711
β_{yyy}	-26.8655776
β_{xxz}	67.8444373
β_{xyz}	-23.3741042
β_{yyz}	40.5162375
β_{xzz}	-28.9147489
β_{yzz}	1.7231059
β_{zzz}	95.5748809
β_{tot}	1.0365619×10^{-30}esu

Vibrational Study

The FT-IR spectrum of LPT is shown in Figure 2 & 3. The broad envelope between 3300 and 2300 cm^{-1} includes absorption of stretching bands due to NH_3^+ion of the amino acid. This region results from superimposed O–H and NH_3^+ stretching bands. It is noted from the spectrum that the bands at 3320 and 3270 cm^{-1} evidence the presence of weakly hydrogen bonded N-H groups. The characteristic OH vibrations of tartaric acid alcoholic group and COOH group are seen to get overlap with the NH vibrations of proline. The band at 2981 cm^{-1} corresponds to broad symmetric stretching of CH_2. The C-O and C=O stretching modes produce peaks at 2749 and 1738 cm^{-1}. Multiple fine structures at the lower energy mode of the envelope indicates the strong hydrogen bonding interaction of NH_3^+ group with strong absorptions of COO^- group at 1576 cm^{-1}. The C-O stretching mode is observed at 1304 cm^{-1}. The CH_2 wagging, twist and rocking modes produce peaks at 1259, 1133 and 835 cm^{-1}, respectively. Further medium band observed at about 1064 cm^{-1} is due to C-Nstretching.

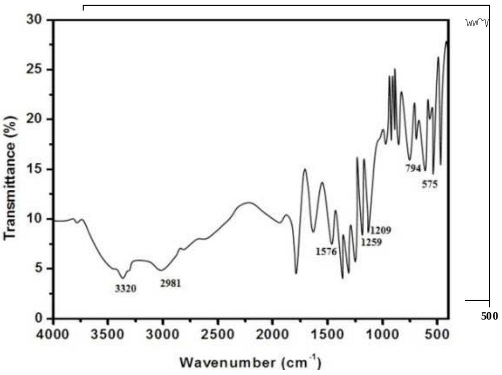


Fig 2 & 3 Experimental and Theoretical FTIR spectrum of LPT

Table 2. Vibrational Assignments

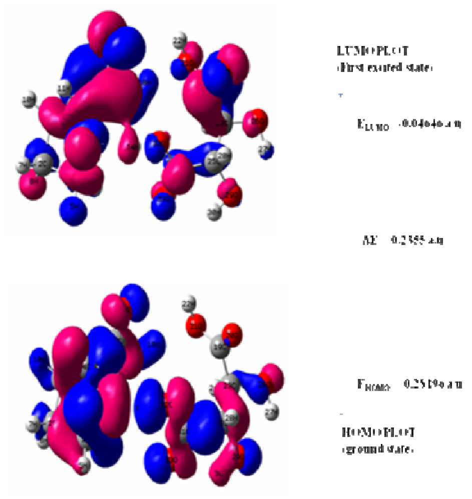
ExperimentalWavenumber (cm^{-1})	**Theoretical 6-31+ G (d,p)**	**Assignment**
3320	3330	N–H stretching
3270	3285	N–H stretching
2981	3019	CH$_2$ symmetric stretching
2749	2761	C=O stretching
1576	1583	COO asymmetric stretching
1410	1421	C–H rocking
1304	1306	C–O stretching
1259	1259	CH$_2$ wagging
1209	1218	COO stretching
1133	1143	CH$_2$ twist
1064	1067	C–N stretching
835	858	CH$_2$ rocking
794	820	N–H deformation
690	697	COO$^-$ scissor
575	579	C–C deformation

The N-H deformation (794 cm^{-1}), COO- scissoring (690 cm^{-1}) and the C-C deformation (575 cm^{-1}) vibrations are also observed. The observed vibrational frequencies and their tentative assignments are listed in Table 2. It is found that theoretically obtain values are higher than experimentally obtained frequencies. This is becauseisolated LPT molecule is used in theoretical calculation.

HOMO-LUMO

The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron.The energy gap between HOMO and LUMO is a critical parameter in determining molecular electrical transport properties. This Electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). While the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity[7].

The LUMO as an electron acceptor represents the ability to obtain an electron, and HOMO represents the ability to donate an electron[8].



NLO studies

For the SHG efficiency measurements, microcrystalline material of KDP was used for comparison. When a laser input of 10.8mJ was passed through LPT, second harmonic signal of 532 nm is produced. Then each tube was held within an optical system that collects all the scattered SHG. The generated SHG output signals were monochromated and monitored by a photomultiplier tube and a digital oscilloscope assembly. The second harmonic signal of 71 mV was obtained for LPT with reference to KDP (53 mV). Thus, the SHG efficiency of LPT is nearly 1.3 times higher than KDP.

Conclusion

Theoretical spectral frequencies are in good agreement with experimental data of FT-IR. The HOMO-LUMO energy gap strongly supports the presence of intramolecular energy transfer within the molecule. The calculated first order hyperpolarizability is 1.0365 x 10^{-30}esu.

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