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Density functional theory and dielectric studies of L- Prolinium Picrate

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INTRODUCTION

In the recent past, organic molecular nonlinear optical (NLO) materials have been appropriately investigated due to their high performance with respect to electro-optic effect as compared to inorganic NLO materials. Organic NLO material serves an important role in second harmonic generation (SHG), frequency shuffling, under water treatment and in medical applications [1, 2]. In recent trend, the amino acid crystals have been grown and their NLO significances are subjected to extensive investigation by several researchers for various applications.Over the past two decades much attention has been paid to the search of novel high quality NLO materials that can generate high second order optical nonlinearities which is important for potential applications including telecommunication, optical computing, and optical data storage and processing [3-5]. Organic NLO materials are formed by weak Van der' Waals and hydrogen bonds with conjugated π electrons and are more advantageous than their inorganic counterparts due to high conversion efficiency for second harmonic generation and transparency in the visible region, high resistance to optical damage and so on. They also offer the flexibility of molecular design and the promise of virtually an unlimited number of crystalline structures. Traditionally, crystals of organic materials have been grown from the melt or from vapor or solution. Ab initio and DFT calculations have been performed to support our wave number assignments [6].

RESULTS AND DISCUSSION

2.1 Powder X-ray Diffraction

Powdered XRD spectrum of the crystals is recorded using Rich Seifert & Co diffractometer with CuKα radiation to identify the compound. From the XRD data, it is found that L-Prolinium Picrate belongs to the Monoclinic system with a = 9.202Å, b= 5.834 Å and c= 13.0874 Å, the space group being P21 and has four molecules in the unit cell with a volume of 702.589 Å^3. The close agreement with the calculated and reported values confirms the identity of the grown crystal. The recorded powder XRD pattern is given in Figure 1.

2.2 Hyperpolarizability

Experimental measurements and theoretical calculations on molecular hyperpolarizabilityβ 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. It also 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 π-systems, and by evaluating the effects of various electron-donor and electron-acceptor groups [7]. The calculated first order hyperpolarizability values for LPOP molecule are given in Table 1. The calculated first order hyperpolarizabilityof LPOP for basis set is9.99235 x 10^{-30}esu the compound having higher β_{tot} value, correspond to low HOMO-LUMO energy gap. This result indicates that intermolecular hydrogen bonds have a substantial influence on the first hyperpolarizability.

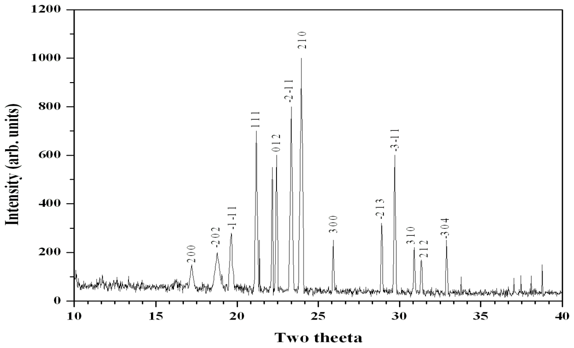


Figure 1. Experimentally obtained Powder XRD pattern of LPOP

2.3 HOMO – LUMO Gap

Molecular orbitals (HOMO and LUMO) and their properties such as energy are very useful for physicists and chemists and are very important parameters for quantum chemistry. This is also used by the frontier electron density for predicting the most reactive position in π electron systems and also explains several types of reaction in conjugated system

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. The energy gap between HOMO and LUMO explains the biological activityof the molecule, which is due to the change in partial charge and to the change in total dipole moment. The plots of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are shown in Fig. 2. This electronic absorption corresponds to the transition from ground to the first excited state and is mainly described by electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

Table 1. The electric dipole moment μ, the average polarizabilityα_{tot} and First hyperpolarizability β_{tot} for LPOP

Para	B3LYP/ 6-31G
Hyperpolarizability	
β_{xxx}	919.31098
β_{xxy}	403.08578
β_{xyy}	89.632383
β_{yyy}	44.731194
β_{xxz}	-349.7647
β_{xyz}	133.99292
β_{yyz}	-24.46061
β_{xzz}	12.651251
β_{yzz}	144.90725
β_{zzz}	548.83836
β_{tot}	9.99235×10^{-30}

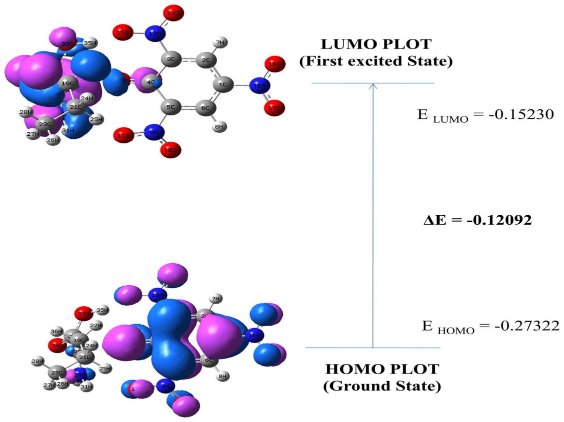


Figure 2. HOMO –LUMO plot of LPOP at B3LYP/6-31G (d, p)

While the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity.

The HOMO and LUMO energy calculated by B3LYP/6-31+ G (d, p) basis set is given below

HOMO energy	-0.27322
LUMO energy	-0.15230
HOMO – LUMO	-0.12092

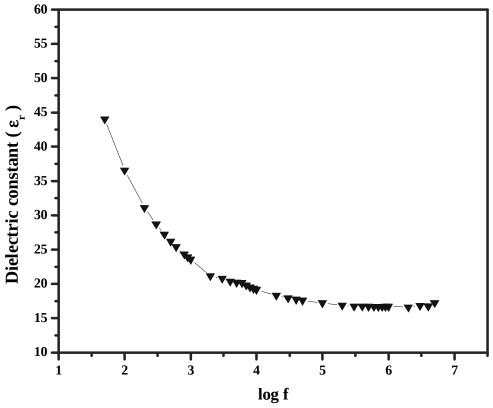
2.4 SHG in LPOP crystal

The freshly powdered sample of particle size (above 150 μm) was illuminated using Q–switched, mode locked Nd: YAG laser with input pulse of 6.2 mJ. The second harmonic (SHG) test by the Kurtz technique confirmed the NLO property of the grown LPOP single crystal [8]. For a laser input pulse of 6.2 mJ, the second harmonic signal (532 nm) of 40.32 mW and 2217.6 mW were obtained through KDP and POP samples respectively. Thus the SHG efficiency of LPOP is 55 times higher than KDP. Since a large molecular hyperpolarizability γ is the basis of a strong second harmonic generation (SHG) response, organic molecules that usually exhibit large γ values are certainly candidate molecules for NLO applications.

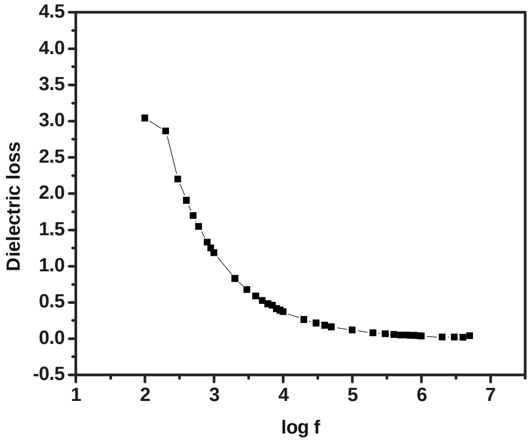
2.5 Dielectric Studies

The electric properties of dielectric substances are usually described in terms of the dielectric constant. For most materials, this quantity is independent of the strength of the electric field over a wide range of the latter, but in the case of alternating fields, it depends on the frequency. Figure 3 show the plots of dielectric constant against log frequency for LPOP crystal. The dielectric constant $\varepsilon_r$at low frequencies depends on the excitation of bound electrons, lattice vibrations, dipole orientations and space-charge polarization. At very low frequencies all four contributions may be active. It is observed that the dielectric constant $\varepsilon_r$decreases with increase in frequency. The large value of dielectric constant at low frequency is due to the presence of space charge polarization. The space charge contribution depends on the purity and perfection of the material. Its influence is mainly noticeable in the low frequency region

Figure 4 show the variation of dielectric loss with log frequency for pure and doped LPOP single crystals. It is observed that the dielectric loss decreases with increase in frequency in the case of all samples. The low values of dielectric loss suggest that the grown crystals are of good quality. In the lower frequency region, dielectric loss shows larger values due to the loss associated with ionic mobility.



Variation of dielectric constant of LPOP



Variation of dielectric loss of LPOP

CONCLUSION

Powder XRD studies show that the grown crystal belongs to monoclinic crystal system having non-centrosymmetry with $P2_1$ space group. Optimized structure of the isolated LPOP molecule obtained by DFT calculations give the minimum energy state. First order hyperpolarizability of LPOP is calculated by two different basis sets and found useful in molecular designing. Frontier molecular orbital analyses give the HOMO-LUMO energy gap value. SHG efficiency of the grown crystal shows that it has 55 times greater than KDP. Low dielectric constant and dielectric loss of LPOP confirms the polarizing ability and hence NLO nature.

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