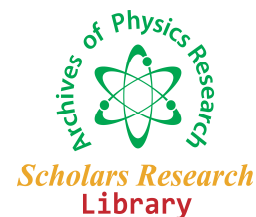




## Scholars Research Library

Archives of Physics Research, 2015, 6 (2):13-17  
(<http://scholarsresearchlibrary.com/archive.html>)



Scholars Research  
Library  
ISSN : 0976-0970  
CODEN (USA): APRRC7

### Spectroscopic investigations on L- Prolinium picrtate

C. Maria Ashok Kumar<sup>1</sup>, S. Arulmozhi<sup>1</sup>, J. Madhavan<sup>1</sup> and G. Prabakaran<sup>2\*</sup>

<sup>1</sup>Department of Physics, Loyola College, Chennai

<sup>2</sup>Department of Physics, Govt. Arts College for Men, Nandanam, Chennai

---

#### ABSTRACT

FT-IR spectrum of L- Prolinium Picrate (LPOP) molecule has been recorded in the region 4000–400 cm<sup>-1</sup>. Optimized geometrical structures, harmonic vibrational frequencies, intensities, reduced mass and force constants have been computed by the B3 Based (B3LYP) density functional method using 6-31+G(d, p) basis set. The observed FT-IR vibrational frequencies are analyzed and compared with theoretically predicted vibrational frequencies. The geometries and normal modes of vibration obtained from DFT method are in good agreement with the experimental data. Second harmonic generation (SHG) efficiency of the grown crystal has been studied using Nd:YAG laser.

**Keywords:** FTIR, NLO, B3LYP

---

#### INTRODUCTION

Amino acid crystals usually display large nonlinear optical (NLO) response and are potential candidates for applications in the emerging areas of photonics. Molecules that show asymmetric polarization induced by electron donor and acceptor groups are responsible for electro optic and NLO properties. 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. Organic NLO materials are formed by weak Vander Waals and hydrogen bonds with conjugated  $\pi$  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 [1-3].

Spectroscopy deals with interaction of matter with electromagnetic energy and spectroscopists harvest wealth of information, about the matter, from these interaction. Molecular spectroscopy aims to understand the interaction of molecular energy with electromagnetic radiation. A molecule possesses various forms of energy due to its different kinds of motion and intermolecular interactions. For instance, it possesses translational energy, rotational energy, vibrational energy, etc., and these energies are quantized and interactions between them are very weak. Electromagnetic radiations can be allowed to interact with the molecular energy levels and investigation of these interactions can provide various information regarding their rotation, charge localization, molecular structure, symmetry, vibration, etc. It is an established fact that the interaction of electromagnetic energy with the vibrational energy levels of a molecule provide amazing information on the molecular dynamics [4-7] and vibrational spectroscopy emerged with theories and techniques to deal with such interactions. Based on the obtained

experimental results, we have proposed the vibrational spectral studies of the molecules using DFT methods. Vibrational spectroscopy involves different methods, the most important of which are infrared spectroscopy.

## MATERIALS AND METHODS

### 2. EXPERIMENTAL DETAILS

L-Prolinium Picrate is synthesized from equimolar solution of L - Proline and Picric acid by slow evaporation. The solubility data was determined by dissolving the synthesized salt of LPOP in 100 ml of mixed solvent of double distilled water and acetone at a constant temperature. The solubility of LPOP increases with the temperature and thus exhibit positive solubility coefficient. Transparent yellow color single crystals were obtained from the re-crystallization salt. Seed crystal is then placed in its supersaturated solution kept in a bath at ambient temperature. Seed crystals are grown to big crystals by slow evaporation to a size of about  $14 \times 2 \times 5 \text{ mm}^3$  with good transparency in a time of about three weeks (Fig.1).



Fig 1. Photograph of LPOP crystal

#### 2.1 Spectroscopic measurements

Infrared spectroscopy is effectively used to identify the functional groups and to determine the molecular structure of the synthesized compound. In order to analyze qualitatively the presence of functional groups in L- Prolinium Picrate, FT-IR spectrum was recorded using Bruker FT-IR Spectrometer by KBr pellet technique in the range  $400\text{--}4000 \text{ cm}^{-1}$ .

#### 2.2 Computational Studies

Quantum chemical density functional theory calculations were carried out with the 2009 version of the Gaussian program package [8] using B3LYP functions combined with the 6-31+G (d, p) basis set. The Cartesian representation of the theoretical force constants has been computed at standard as the optimized geometry by assuming Cs point group symmetry (low symmetry). The optimized geometrical parameters, fundamental vibrational frequencies, IR intensity, Raman activity, the atomic small charges, Dipole moment, reduced mass, force constant and other thermodynamic parameters were calculated.

## RESULTS AND DISCUSSION

### 3.1 Molecular Geometry

The labeling of atoms of the LPOP is shown in Fig. 2. The global minimum energy is obtained by the DFT structure optimization based on B3LYP with 6-31+G (d, p) is -1321.6719 Hartrees. The optimized geometrical parameters obtained by the large basis sets calculations (the global minimum energy) are used in this study. The structure optimization zero point vibrational energy and nuclear repulsion energy of the LPOP in B3LYP/6-31+G (d, p) is  $668028.0 \text{ Jmol}^{-1}$  Hartrees. The optimized structural parameters such as bond lengths and bond angles by DFT-B3LYP with 6-31+G (d, p) basis set are shown in Table 1.

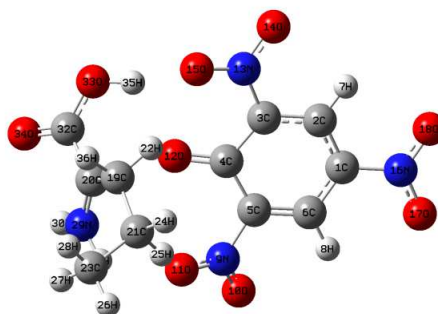


Fig 2. Atomic numbering system adapted for ab initio computations of LPOP molecule

### Vibrational assignments

Vibrational spectral assignments have been performed on the recorded FT-IR spectrum based on the theoretically predicted wavenumbers by density functional method (B3LYP/6-31+G (d, p)) have been presented. There are 102 normal modes of fundamental vibrations which span the irreducible representations. The detailed vibrational assignments of fundamental modes of LPOP, FT-IR experimental frequencies, calculated frequencies and vibrational assignment by DFT method for 6-31 basis set is reported in Table 2. For comparison, the experimental FT-IR and theoretically simulated spectra were presented in Figs 4, 5 and 6.

Table I. Selected geometrical parameters LPOP computed by using 6-31 G (d, p) basis set

Bond Length (Å)	6-31+ G (d, p)	Bond Angle (°)	6-31+ G (d, p)
C <sub>1</sub> -C <sub>2</sub>	1.39202	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	119.55744
C <sub>2</sub> -C <sub>3</sub>	1.39010	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	122.86610
C <sub>4</sub> -C <sub>5</sub>	1.45805	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	113.29239
C <sub>1</sub> -N <sub>16</sub>	1.45163	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	123.22036
C <sub>4</sub> -O <sub>12</sub>	1.27679	C <sub>5</sub> -C <sub>6</sub> -C <sub>1</sub>	119.34398
N <sub>9</sub> -O <sub>10</sub>	1.26450	C <sub>6</sub> -C <sub>1</sub> -N <sub>16</sub>	119.29547
N <sub>9</sub> -O <sub>11</sub>	1.27383	O <sub>17</sub> -N <sub>16</sub> -O <sub>18</sub>	124.11108
N <sub>13</sub> -O <sub>14</sub>	1.26178	C <sub>1</sub> -N <sub>16</sub> -O <sub>18</sub>	118.02602
N <sub>13</sub> -O <sub>15</sub>	1.28557	C <sub>3</sub> -N <sub>13</sub> -O <sub>14</sub>	118.87385
N <sub>16</sub> -O <sub>18</sub>	1.26615	C <sub>3</sub> -C <sub>4</sub> -O <sub>12</sub>	123.36249
N <sub>16</sub> -O <sub>17</sub>	1.26682	H <sub>31</sub> -N <sub>29</sub> -H <sub>30</sub>	117.84107
C <sub>32</sub> -O <sub>34</sub>	1.23568	H <sub>35</sub> -O <sub>33</sub> -C <sub>32</sub>	117.33103
C <sub>32</sub> -O <sub>33</sub>	1.33024	C <sub>23</sub> -C <sub>21</sub> -H <sub>24</sub>	108.44630
C <sub>20</sub> -N <sub>29</sub>	1.29837	C <sub>32</sub> -C <sub>20</sub> -N <sub>29</sub>	114.09023

### C-C vibrations

The bands between 1400 and 1650 cm<sup>-1</sup> are due to C-C stretching vibrations in benzene [9-10]. The carbon-carbon stretching modes of the phenyl group are expected in the range from 1650 to 1200 cm<sup>-1</sup>. The actual position of these modes is determined not so much by the nature of the substituent but by the form of substitution around the ring [11]. In general, the bands of stretching, wagging and deformation are of variable intensity and are observed at 1600-1400 cm<sup>-1</sup>, 400-500 cm<sup>-1</sup> and 100-300 cm<sup>-1</sup>. Experimental value for C-C vibrations of LPOP molecule was observed at 1538, 1449 and 1428 cm<sup>-1</sup>. C-C in-plane and out-of-plane deformed vibrations are the modes associated with smaller force constants than the stretching ones, and hence assigned to lower frequencies. C-C in plane deformed vibrations are observed at 108.6421, 299.9733, 314.5973 cm<sup>-1</sup> by B3LYP method with 6-31+ G (d, p) basis set. C-C wagging vibrations for this molecule are assigned at 435.3246 cm<sup>-1</sup> with 6-31+ G (d, p) basis set. It's found from the calculation that the approximation of orbitals in the basis set 6-31+G (d, p) were done to nearer the calculated values to experimental values. Experimental values for C-C vibrations like stretching, wagging, deformation are very closer to calculated values.

### Nitro group vibrations

Aromatic nitro compounds have strong absorptions due to asymmetric and symmetric stretching vibrations of the nitro group at 1570-1485 cm<sup>-1</sup> and 1370-1320 cm<sup>-1</sup> [12]. The symmetric NO<sub>2</sub> stretching is observed in IR as a medium band at 1335.35 cm<sup>-1</sup> by B3LYP method with 6-31+ G (d, p) basis set and from the experimental spectrum it is observed at 1334 and 1080 cm<sup>-1</sup>. The experimental values are in good agreement with the computed values. The

nitro group is capable of bending in a number of different directions and these vibrations give rise to several variable intensity bands at lower wave numbers. The NO<sub>2</sub> torsion and scissoring vibrations are obtained at 43.534, 545.669 cm<sup>-1</sup> with 6-31+ G (d, p) basis set. The medium band in IR at 752 cm<sup>-1</sup> is assigned to the NO<sub>2</sub> scissoring mode by B3LYP method with 6-31+G (d, p) basis set. The bands obtained at 722.541 cm<sup>-1</sup> are assigned to open plane deformation of LPOP by B3LYP method with 6-31+ G (d, p) basis set.

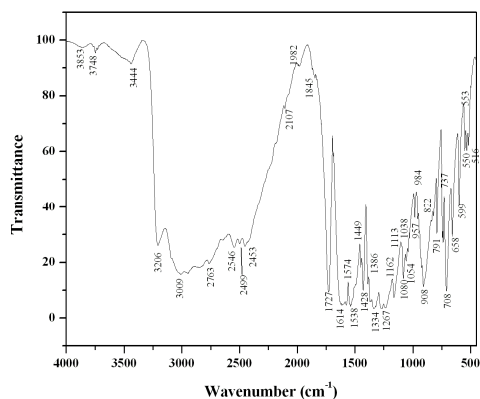


Fig. 3 Experimental FT-IR

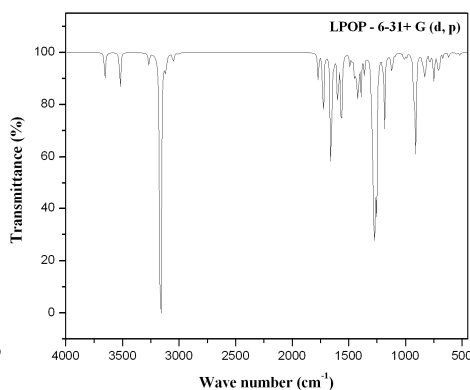


Fig 4.Observed FT IR Spectrum by 6-31+ G (d, p)

### C-N Vibrations

The C-N ring stretching vibration bands occur in the region 1600 - 1500 cm<sup>-1</sup>. The present molecule exhibits this vibration in IR spectrum at 1449 cm<sup>-1</sup> and the theoretically computed value at 1451.94cm<sup>-1</sup> by 6-31+ G (d, p) method shows good agreement with recorded spectrum. C-N stretching absorption assigned in the region 1382–1266 cm<sup>-1</sup> [13]. In the present work, the band observed at 1012 cm<sup>-1</sup> in FT-IR spectrum has been assigned to C-N stretching vibration. The calculated frequency at 362cm<sup>-1</sup>by 6-31+ G (d, p) is in good agreement with experimental value. Calculated band at 82.439 and 83.296 cm<sup>-1</sup> is assigned to CN in plane bending.

Table 2.Selected Experimental and Calculated B3LYP/6-31 level of vibrational frequencies of LPOP

FT-IR	B3LYP- Calculated frequency	Calculated IR intensity	Force Constants	Vibrational Assignments
3444	3522.5416	114.9461	7.6285	N-H str
3206	3265.7497	18.3360	6.7321	C-H v
3009	3007.9345	3.2527	5.6349	CH <sub>2</sub> v
1845	1770.1516	69.8215	3.5264	C =C st
1727	1724.4108	263.3822	10.8281	CC st
1614	1626.7512	26.1290	2.9178	C=C v
1574	1565.0354	313.2407	1.5624	Ph I
1538	1544.9859	4.7475	8.3631	C-C v
1449	1451.4283	34.2571	16.7987	CH <sub>3</sub> ben
1428	1434.8873	89.5762	12.9493	C-C v
1386	1391.3814	113.8645	3.9736	C-H v
1334	1335.3147	10.2417	1.3152	NO <sub>2</sub> str
1267	1266.7543	519.5657	7.4672	Ph I
1162	1180.7366	201.7162	2.0298	NH <sub>2</sub> v
1113	1115.4315	80.1294	1.2685	C-N
1080	1087.5427	7.7959	1.7426	N-O <sub>2</sub> str
908	908.1271	281.6870	0.7850	CH d
737	747.2678	74.9418	1.0696	CH st
708	709.9594	23.5482	3.5208	CH opb
658	669.9687	13.9271	2.9933	Ph I + CH str
553	553.2374	3.7620	1.6200	OC bend
516	519.6399	7.2054	0.4981	CH ipd

*St*-stretching ; *symst*- symmetry stretching ;*asyst*- asymmetry stretching ;*sci*-scissoring; *t*-twisting ;*ipb*-in-plane bending ;*opb*- out-of-plane bending;*ipd*-inplane deformation *wag*- wagging; *R*-anthracene ring;; *roc*-rocking;*I*-Ortho; *II*-para substituted.*de*-deformation

### 4. Second Harmonic Generation

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 [14]. 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 LPOP samples respectively. Thus the SHG efficiency of LPOP is 55 times higher than KDP.

### CONCLUSION

Single crystals of LPOP are conveniently grown by employing slow evaporation technique in a period of three weeks. Optimized structure of the isolated LPOP 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. Theoretical and experimental Spectroscopic studies exemplify the presence of various functional groups in the molecule. Both theoretically simulated and experimentally obtained FT-IR spectra show coincidence. The powder SHG analysis reveals that the efficiency of this material is 55 times that of KDP.

### REFERENCES

- [1] T. Sujatha, A. CyraPeter, M. Vimalan, J. Merline Shyla, J. Madhavan, *Physica B*, **2010**, 3365–3370.
- [2] S. Tamilselvan, M. Vimalan, I. VethaPotheher, S. Rajasekar, R. Jeyasekaran, M. Antony, J. Madhavan, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **2013**, 114, 19-26.
- [3] D. Sankar, Vinay Raj Menon, P. Sagayaraj, J. Madhavan, *Physica B: Condensed Matter*, **2010**, 405, 192-197.
- [4] S. Arulmozhi, M. Victor Antony Raj and J. Madhavan, *Der Chemica Sinica*, **2011**, 6, 158-163.
- [5] M. Victor Antony Raj, J. Madhavan, M. Gulam Mohamed, *J. Comput. Method. Mol. Design*, **2011**, 4, 57-64.
- [6] HaciOzsisik, SemranSaglam, Sevgi Haman Bayari, *Structural Chemistry*, **2008**, 19, 41-50.
- [7] ŞenayYurdakul, SibelTanrıbuyurdu, *Structural Chemistry*, **2012**, 23, 433-440.
- [8] M.J.Frisch, et al., Gaussian 03, Revision C.02, Gaussian Inc., Wallingford, CT, **2004**.
- [9] V. Krishnakumar, R. John Xavier, *Indian J. Pure. Appl. Phys.*, **2003**, 41, 95.
- [10] N. P. Singh, R. V. Yadav, *Indian J. Phys. B*, **2001**, 75, 347.
- [11] L. J. Bellamy, *The IR spectra of Complex Molecules.*, John Wiley and Sons, NY, **1975**.
- [12] T. Vijayakumar, I. Hubertjoe, C. P. R. Nair, V. S. Jayakumar, *Chem. Phys.*, **2008**, 343, 83.
- [13] Shanmugam, Sathyanarayana., *Spectrochim. Acta.*, **1984**, 40, 757.
- [14] S. K. Kurtz, and T. T. Perry, *J. Appl. Phys.*, **1968**, 39, 3798.