Crystal Structure, Vibrational Spectra and Theoretical Studies on Glycine Lithium Sulphate

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Abstract. In this work we present structural and FT-IR studies on the nonlinear semi organic molecular crystal Glycine Lithium Sulphate (GLS). Vibrational spectral measurements were made for GLS. Optimized geometrical structure and harmonic vibrational frequencies were computed by DFT (B3LYP) method using 6-31++G (d, p) basis set. Complete assignments of the observed spectra were proposed. To investigate microscopic second order nonlinear optical behavior of the examined complex the electric dipole, the polarizability and the first order Hyper polarizability were computed.

1. INTRODUCTION
Recently several studies dealing with organic, inorganic and semi organic materials possessing nonlinear properties are being reported due to the increasing need for photonic applications [1]. In this work, the growth and characterization of Glycine Lithium Sulphate by slow evaporation method from aqua solution are reported. Also Literature survey shows that computation studies have not been done so far on the title compound. The aim of this study is to give a complete description of the molecular geometry and molecular vibrations of the GLS.

2. EXPERIMENTAL DETAILS
Glycine Lithium Sulphate crystal were synthesized by taking Analytical grade of Glycine and Lithium Sulphate in the molar ratio and dissolved in double distilled water.

\[ \text{C}_2\text{H}_5\text{NO}_2 + \text{Li}_2(\text{SO}_4) \rightarrow \text{Li}_2(\text{SO}_4)(\text{C}_2\text{H}_3\text{NO}_2) \]

Based on the solubility data as shown in Figure.1 supersaturated solution of GLS was prepared and stirred well for 3 hours. The beaker containing solution was kept in the constant temperature bath and tiny crystals of GLS were observed at the bottom of the beaker. The transparent tiny crystals were chosen as the seeds for growing bulk crystals. Crystals of size 10 x 11 x 12 mm³ were harvested and is as shown in Figure.2. The grown sample was subjected to powder XRD analysis and its lattice parameters were calculated.
3. RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis
From the powder x-ray diffraction analysis, it was observed that the crystal belongs to orthorhombic crystal system having non-centro symmetric with Pna2₁ space group. The crystal data are given in Table 1. The recorded powder XRD pattern is given in Figure 3.

3.2 Computational Details
All calculations are performed using Gaussian03 program package. Vibration frequencies are calculated using B3LYP/631(d,p) [2,3]. Vibration mode assignments were also compared with the
experimental results. The optimized geometrical parameters, fundamental vibrational frequencies, IR intensity, reduced mass, and force constant were calculated.

| Crystal Parameters of GLS |
|---------------------------|
| **Empirical formula**     | C_2H_5Li_2N_6O_6S |
| **Crystal System**        | Orthorhombic     |
| **Space Group**           | Pna2_1            |
| **a(Å)**                  | 16.423           |
| **b(Å)**                  | 5.0050           |
| **c(Å)**                  | 7.654            |
| **β(°)**                  | 629.1            |

Figure 3. Powder XRD spectrum of GLS crystal

3.3 Molecular Geometry
The atomic numbering scheme for GLS is shown in Figure 4. The most optimized geometric parameters (bond length and bond angles) were calculated and were depicted in Table 2. From the theoretical values, the most optimized bond lengths are slightly shorter as well as longer than the experimental values. Many researchers explained the changes in bond length of the C-H bond on substitution due to a change in the charge distribution on the carbon atom of the benzene ring [5]. The experimental values of C_4-H_5 bond length is longer than the theoretical values. A notable difference among the methods occurs in the computed N_7-H_8, H_10-Li_11, N_7-Li_11 and O_15-O_17 bond lengths. The DFT gives bond angle O_2-C_1-O_3 = 120, H_8-N_7-H_9=109.47 and N_7-O_12-Li_11=135.2 whereas the
corresponding XRD values are 124.267, 108.58 and 134.645 respectively. The comparison of Table 2. reveals the DFT calculation describes the geometry of the crystal with good quality.

Figure 4. Atomic numbering system adapted for ab initio computations of GLS molecule

Table 2. Selected bond lengths and bond angles of GLS molecule

| S.No | Molecule     | Bond length (Å) | Molecule     | Bond angles (°) |
|------|--------------|-----------------|--------------|----------------|
| 1    | C₁-O₂        | 1.430000        | O₂-C₁-O₃     | 120            |
| 2    | O₂-O₃        | 2.476833        | C₁-C₄-H₆     | 109.4712       |
| 3    | O₂-Li₁₁      | 1.89            | H₉-N₇-O₁₂    | 118.5122       |
| 4    | C₄-H₅        | 1.07            | H₆-N₇-H₉     | 109.4712       |
| 5    | H₅-N₇        | 2.086720        | O₂-C₁-C₄     | 120            |

3.4 Vibrational Assignments

The Fourier Transform Infra Red spectra of GLS was recorded on IFS 66V FT-IR SPECTROMETER using KBr pellet in the range 4000 cm⁻¹ to 500 cm⁻¹. The observed FT-IR is shown in Figure 5. The GLS molecule has 17 moieties and is in stable conformation with C₁ symmetry then exhibits 45 normal modes of vibrations. The normal modes of GLS is distributed amongst the symmetry species as

\[ \Gamma_{3N-6} = 31A' \text{ (in-plane)} + 14A'' \text{ (out-of-plane)} \]
Nitrogroup vibrations
Aromatic nitro compounds have strong absorptions due to asymmetric and symmetric vibrations of the nitro group at 1570-1485 cm$^{-1}$ and 1370-1320 cm$^{-1}$ [4,5]. The theoretical asymmetric stretching vibrations occur at 1503 cm$^{-1}$ and the corresponding experimental peak at 1571 cm$^{-1}$.

C=O vibrations
The stretching vibration C=O is commonly expected in the region 1690±30 cm$^{-1}$. The C=O in-plane deformation is expected in the region 645±55 cm$^{-1}$. The C=O out-of-plane deformation is in the range 540±80 cm$^{-1}$. The theoretical stretching vibration appears at 1679 cm$^{-1}$ and the in-plane deformation at 653 cm$^{-1}$ (theoretical) and 649 cm$^{-1}$ (experimental).

C=N vibrations
According to Henry et al (2008), IR spectrum exhibits strong and broad bands due to C=N at 1635 cm$^{-1}$. In the present work the theoretical and experimental strong and broad bands due to C=N appears at 1626 cm$^{-1}$ and 1645 cm$^{-1}$ respectively.

The selected vibrational assignments of fundamental modes of GLS by DFT methods are reported in Table 3.

| No. | Wavenumber cm$^{-1}$ | Spectroscopic assignment | Force constant | Reduced mass |
|-----|----------------------|--------------------------|----------------|--------------|
| B3LYP | Expt. | assignment |          |              |
| 1.   | 457.3058 | 457 | COO’ opd | 1.7983 | 14.5946 |
| 2.   | 520.3388 | 527 | COO’ d   | 1.8572 | 11.6421 |
| 3.   | 653.1643 | 649 | COO’ roc ipd | 1.7693 | 7.0388 |
| 4.   | 897.9603 | 895 | CC st    | 2.4910 | 5.2433 |
5. 970.3730   995      CN st    0.9178   1.6543
6. 1050.167   1099     I Ph     2.1834   3.3602
7. 1183.694   1165     CH₂ roc  1.3022   1.5774
8. 1449.395   1492     COO’ symst 1.4858   1.2004
9. 1503.990   1571     NH₃⁺ sym d 1.7639   1.3236
10. 1626.886  1645     NH₃⁺ asy d 1.6559   1.0619

Symst-symmetric stretching, asyst-asymmetric stretching, st(ph)-stretching of phenyl, roc-rocking, opb-out of plane bending, opd-out of plane deformation, wag-wagging, ipd-in plane deformation, d-deformation

3.5 Hyperpolarizability
First hyperpolarizability is a third rank tensor that can be described by a 3x3x3 matrix. The 27 components of this 3D matrix can be reduced to 10 components due to Kleinman symmetry [6]. In the presence of applied electric field, the energy of a system is a function of electric field. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field[7]. The first static hyperpolarizability (β₀) and its related properties have been calculated using B3LYP/6-31G level based on finite field approach. The calculated dipole moment(μ), polarizability(α) and first order hyperpolarizability values for GLS molecule are given in Table 4.

| Dipole Moment in Debye | Polarizability in esu | Hyperpolarizability in esu |
|------------------------|-----------------------|---------------------------|
| μₓ                    | αₓ  67.4945318        | βₓₓₓ  339.8812369        |
| μᵧ                    | αᵧ  0.9920316         | βᵧᵧᵧ  68.9682643         |
| μₜₒ                  | αₜₒ -4.5362599       | βᵧᵧᵧ  268.4342981        |
| αₓᵧ                   | βₓᵧ  6.6848818        | -78.79471                |
| αᵧᵧ                   | βᵧᵧ  85.163995        | -16.2330359              |
| αₒ  5.9043 x 10⁻³¹    | βᵧᵧᵧ  5.503936        |                           |
| βₓₓ       140.9210373  |                       |                           |
| βᵧᵧ       151.7801336  |                       |                           |
| βᵧᵧᵧ      -114.5418743 |                       |                           |
| βₜₒ      6.7368 10⁻³⁰  |                       |                           |

3.6 Hyperpolarizability
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presence of applied electric field, the energy of a system is a function of electric field. The components of $\beta$ are defined as the coefficients in the Taylor series expansion of the energy in the external electric field[7]. The first static hyperpolarizability ($\beta_0$) and its related properties have been calculated using B3LYP/6-31G level based on finite field approach. The calculated dipole moment($\mu$), polarizability($\alpha$) and first order hyperpolarizability values for GLS molecule are given in Table 4.

3.7 HOMO-LUMO energy gap
HOMO and LUMO analysis have been used to elucidate the information regarding charge transfer within the molecule. The intermolecular charge transfer from the donor to acceptor group through a single-double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability. The HOMO and LUMO energy calculated by B3LYP/6-31G (d,p) method as shown in Figure 5.

HOMO energy (B3LYP) = -0.336 a.u.
LUMO energy (B3LYP) = -0.157 a.u.
HOMO–LUMO energy gap (B3LYP) = 0.179 a.u.

![HOMO–LUMO plot of GLS at B3LYP/6-31 G (d, p)](image)

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

4. CONCLUSION
Good optical quality bulk single crystal of GLS has been grown successfully by slow evaporation growth technique. The single crystal analysis shows that the crystal belongs to orthorhombic crystal system with Pna2$_1$ space group. DFT computations of GLS molecule calculated by DFT (B3LYP) level with 6-31G (d,p) basis set gives the optimized structure. Experimentally obtained bond lengths and bond angles are compared with theoretically calculated one. Theoretical and experimental IR spectroscopic analysis was carried out and the presence of functional groups in GLS molecule was qualitatively analyzed. Nonlinear optical NLO behaviour of the examined sample was investigated by the determination of the electric dipole moment $\mu$, the polarizability $\alpha$ and the hyperpolarizability $\beta$ using DFT method. HOMO-LUMO analysis reveals the molecular energy gap.
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