Sciencia Acta Xaveriana
An International Science Journal
ISSN. 0976-1152

Volume 4
No. 2
pp. 51-58
September 2013

First Order Hyperpolarizability and Homo-Lumo Analysis of L-Arginine Maleate (LArM) by Density Functional Theory Methods

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Abstract : Quantum mechanical calculation is an effective tool to study the molecular behavior. L-Arginine maleate(LArM) an efficient NLO material is analyzed quantum mechanically by ab initio and Density Functional(DFT) method. It's found that first order hyperpolarizability of the molecule is 6.30615227×10^{-30}esu and the large value of hyperpolarization along z direction shows a substantial delocalization of charges in these directions. Highest Occupied Molecular Orbital (HOMO) energy and Lowest Unoccupied Molecular (LUMO) energy were calculated and molecular energy gap is found to be 0.04638 a.u. This HOMO is mainly localized on the malate anion so that its energy is indicative of the donating character and LUMO is localized on L- Arginine cation. Strong donating group leads to high Polarizability values. Second Harmonic Generating efficiency depends on high hyperpolarizability of the material.

(Received July 2013, Accepted September 2013)

1.Introduction

Nonlinear optical (NLO) materials showing second harmonic generation (SHG) have been in demand over the last few decades due to technological importance in the fields of optical communication, signal processing, and instrumentation. In the search of new non-linear optical (NLO) materials compared to inorganic materials organic counterparts have high Second Harmonic Generation(SHG) efficiency[1,2] In recent years much effort is being rendered to understand the origin of non-linearity and to relate the NLO responses to electronic structure and molecular geometry for designing and fabricating the NLO materials of large molecular hyperpolarizability. Knowledge of molecular geometry may help researchers to predict the physiochemical properties of the compound material in different enviroinment. Amino acid family of materials exibit high second order generating (SHG) character. In solid state, amino acid contains a deprotonated carboxylic acid group (COO-) and protonated amino group (NH3+). This dipolar nature exhibits peculiar physical and chemical properties in amino acids, thus making them ideal candidates for NLO applications. Some known or novel crystalline salts of L-arginine with inorganic acids were grown and characterized.[3,4] In this present communication, the synthesis, single crystal growth of L-arginine maleate (LAM) from its aqueous solution by slow cooling method has been reported.The title molecule is exposed to, DFT analyses, first order hyperpolarizability studies,HOMO –LUMO analysis and second harmonic generation efficiency measurements.

2. Material Synthesis and Crystal Growth

Equimolar amount of strongly basic amino acid, L-arginine (Merck, 99%) and weak organic acid, maleic acid (Loba Chemie, 99.5%) were dissolved in double distilled water to synthesize LArM . During this crystallization, L-arginine maleate transformed to its hydrated form with

the addition of two molecules of water of crystallization to its crystal lattice. The synthesized material was then purified by repeated recrystallization process. L-arginine maleate was dissolved in double distilled water and kept in a constant temperature bath with a cryostat facility and stirring was achieved continuously for 8 h.. 200 ml of saturated solution of LArM at 40 °C was prepared and the solution was filtered. Seeds obtained from slow evaporation technique were used for bulk growth. Optical quality crystal with dimension of 25×23×19 mm^3 has been grown over a typical growth period of 3 weeks.Photograph of as grown single crystal is shown in Figure 1.

Figure 1. Photograph of as grown LArM single crystal

3.Hyperpolarizability Studies

The hyperpolarizability and non linear optical properties of an isolated molecule of potential NLO materials are considered as an extensive tool of research in molecular spectroscopy. The length of the conjugated π-electrons are vital factor in contributing to hyperpolarizability. It has been demonstrated that the first order hyperpolarizability increases with the third power of the number ofπ-electron bonds and the correlation of polarizability and hyperpolarizabilities with bond length alternation in the conjugatedπ-electron system from the neutral ground state structure to the resonance structure of a charge-transfer state of the system. This electron cloud makes the molecule highly polarized and the intermolecular charge transfer interaction is highly responsible for the NLO properties of the title compound.

Relation connecting non linear response, linear polarisability(α_{ij}) and first order hyperpolaraisability(β_{ijk}) can be represented as a Taylor expansion of the total dipole moment as

$$\mu_{t} = \mu_{0} + \alpha_{ij}E_i + \beta_{ijk}E_iE_j + \ldots \quad (1)$$

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

$$\beta_{ij} = \beta_{iii} + 1/3 \sum_{i \neq j} \beta_{ijj} + \beta_{jij} + \beta_{jji}) \quad (2)$$

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

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

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

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

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

The first order hyperpolarisability (β_{ijk}) of LAM is calculated using6-31G(d,p) basis set based on finite field approach. Hyperpolarisability is a third rank tensor that can be described by a 3x3x3 matrix. The 27 components of 3D matrix can be reduced to 10 components due to Kleinman symmetry.[5] The calculated first order hyperpolarisability values for LAM molecule are given in Table 1. It is found from the table β_{zzz} value is maximum among the tensor values which indicates that more delocalization of electron could takes place in that particular direction. This may be due to π-electron cloud movement form donor to acceptor which make the molecule highly polarisable an essential behavior for NLO activity.

β_{xxx}	-154.0584244
β_{xxy}	-154.0584244
β_{xyy}	265.3935258
β_{yyy}	-80.3168278
β_{xxz}	1460.1973362
β_{xyz}	-673.076011
β_{yyz}	511.9064268
β_{xzz}	352.2447648
β_{yzz}	334.4451487
β_{zzz}	-2557.9267795
β_{tot}	6.30615227×10^{-30}

Table 1. Hyperpolarizability of LArM molecule

4. HOMO-LOMO Analysis

The interaction of two atomic (or) molecular orbitals produces two new orbitals. One of the new orbital is higher in energy than the original ones (the anti-bonding orbital) and one is lower (the bonding orbital). When one of the initial orbitals is filled with a pair of electrons (a Lewis base) and the other is empty (a Lewis acid), we can place the two electrons into the lower, energy of the two new orbitals. The "filled-empty" orbital interaction therefore is stabilizing. When we are dealing with interacting molecular orbitals, the two that interact are generally the highest energy occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the compound. These orbitals are a pair of orbitals, which allows them to interact most strongly. These orbitals are sometimes called the frontier orbitals, because they lie at the outermost boundaries of the electrons of compound. The intramolecular charge 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, making IR activity strong. The HOMO–LUMO energy gap of LArM was calculated at B3LYP/6-31G(d,p) level, which reveals that the energy gap reflects the chemical activity of the molecule.

HOMO energy = -0.08737 a.u.

LUMO energy = -0.04099 a.u.

HOMO–LUMO energy gap = 0.04638 a.u.

The LUMO as an electron acceptor represents the ability to obtain an electron and HOMO represents ability to donate an electron . The strong charge transfer interaction through π-conjugated bridge results in substantial ground state donor–acceptor mixing and the appearance of a charge transfer band in the electron absorption spectrum

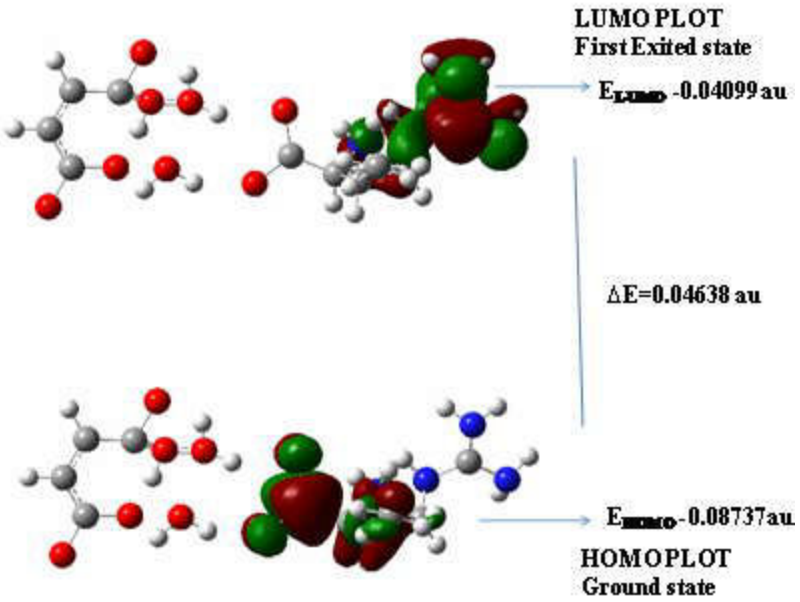

Figure 2. HOMO – LUMO plot of LArM molecule.

5. Second Harmonic Generation (SHG) Efficiency Studies

The NLO properties of the grown crystal is studied, Kurtz and Perry technique[6]. A high-intensity Nd:YAG laser with fundamental radiation of 1064 nm was used as the optical source and directed onto the powered sample of crystal. The SHG behavior has been confirmed

from the output of intense green light emission (k = 532 nm) from the crystal. KDP sample was used as the reference material and Intensity of the bright green emission is 3.8 times higher that of KDP.

6. Conclusion

Single crystals of LArM are conveniently grown by employing slow evaporation technique. First order hyper polarisability of LArM in calculated and found useful in molecular designing. HOMO-LUMO analysis is done for the candidate material using B3LYP/6-31G(d,p) method and its value is found as 0.04638 a.u. SHG efficiency of the grown crystal was confirmed by NLO test and its found that 3.8 times higher that of KDP.

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