Factor group analysis and hyperpolarizability studies of nonlinear optical L-asparaginium picrate (LASP) crystals

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Abstract

The factor group analysis and the hyperpolarizability study were carried out for the L-asparaginium picrate (LASP) single crystals to explore the possible vibrational modes and the microscopic nonlinearity by the density functional triply parameter hybrid model DFT/B3LYP using GAUSSIAN 98W, respectively. The HF/6-31G (d,p) basis set has been employed. The calculated first order hyperpolarizability of LASP is 4.815×10^{-29} esu. The Fourier transform infrared (FTIR) spectroscopic studies were performed for identifying different functional groups present in the compound. © 2008 Elsevier B.V. All rights reserved.

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1. Introduction

Nonlinear optical (NLO) materials utilize the nonlinear dependence of the refractive index on the applied electric field to bring forth other frequencies. The added esteem of nonlinear optical materials over lasers and electro-optics became preponderant from the early days of lasers. NLO materials endow the expansion of the circumscribed spectral regime of lasers. The pursuance for more efficient nonlinear optical (NLO) materials of increased optical quality is being goaded by the development of optical communication systems that require ultra fast broadband optical signal processing functions. The noetic construction of structurally controlled supramolecular assemblies (e.g., acentric and chiral solids) remains a great challenge even though the art of chemical synthesis of discrete molecules has significantly advanced in recent decades. The relevance of organic materials in this perking context is due to the fact that the delocalized electronic structure of π-conjugated organic compound offers a number of tantalizing opportunities in applications as nonlinear optical materials [1–3]. Moreover, organic materials offer flexibility of molecular design, virtually an unlimited number of crystalline structures and a high

damage resistance to optical radiation. Hence, these materials might make it desirable to replace electronic switching circuits in computing and telecommunication systems with purely optical devices [4]. Organic molecules with significant nonlinear optical activity consists of a π-electron conjugated moiety substituted by an electron donor group on one end of the conjugated structure and an electron acceptor group on the other end, forming a 'push–pull' conjugated structure [5]. The conjugated π-electron moiety provides a pathway for the entire length of conjugation under the perturbation of an external electric field. The donor and acceptor groups provide the ground state charge asymmetry of the molecule, which is required for second order nonlinearity. The peculiar physical properties of this interesting class of compounds are governed by the high degree of electronic charge delocalization along the charge transfer axis and by the low band gaps [6,7]. Due to their potential applications in photonic devices, the study of nonlinear optical properties of molecules, and their hyperpolarizabilities is considered as important for extensive research, and lot of efforts taken on the experimental [8,9] and theoretical aspects [10,11] on the bulk NLO properties as well as their dependence on the first order hyperpolarizabilities of molecules. Acentric molecules consisting of highly delocalized π-electron systems interacting with suitably substituted electron donor and acceptor groups exhibit a high value of second order polarizability (β) [12]. L-Asparaginium picrate (LASP) is one such π-donor acceptor molecular compounds in which L-asparagine acts as donor and the picric acid as electron

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acceptor. Anitha et al. has reported the unit cell parameters of the LASP [13]. We have already reported the growth, dielectric, mechanical properties, SHG studies and the effect of irradiation on LASP crystals [14,15].

2. Studies and results

2.1. Hyperpolarizability studies

2.1.1. 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.

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

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

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{i \neq j}(\beta_{ijj} + \beta_{jij} + \beta_{jji}) \tag{2}$$

Using the x, y and z components the magnitude of first order hyperpolarizability (β total) tensor, can be calculated by the following equations.

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

The complete equation for calculating the first order hyperpolarizability from GAUSSIAN 98W output is given as follows [16]

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

The β components of GAUSSIAN 98W output are reported in atomic units, the calculated values have to be converted into electrostatic units (1 a.u. $= 8.3693 \times 10^{-33}$ esu).

2.1.2. Computation details

Before calculating the hyperpolarizability of the compound, the geometry taken from the starting structures based on its crystallographic data was optimized in the UHF (unrestricted open-shell Hartree–Fock) level. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal co-ordinates. All optimized structures were confirmed to be minimum energy conformations. An optimization is complete when it has converged—i.e., when it has reached a minimum on the potential energy surface, thereby predicting the equilibrium structures of the molecules. This criterion is very important in geometry optimization. The inclusion of d polarization and double zeta function in the split valence basis set is expected to produce a marked improvement in the calculated geometry [17]. At the optimized structure no imaginary frequency modes were obtained proving that a true minimum on the potential energy surface was found. The dispersion

Table 1
Hyperpolarizability of LASP in esu

β_{xxx}	3471.39
β_{xxy}	181.20
β_{xyy}	39.10
β_{yyy}	−8.04
β_{zxx}	3198.6
β_{xyz}	126.66
β_{zyy}	−17.68
β_{xzz}	1298.08
β_{yzz}	37.10
β_{zzz}	−370.29
β_{total}	4.8152

Hyperpolarizability $\beta(-2\omega: \omega, \omega)$ in 10^{-29} esu.

free first order hyperpolarizability was calculated using finite field method. The finite field method offers a straightforward approach to the calculation of hyper polarizabilities [18]. All the calculations were carried out by the Density Functional triply parameter hybrid model DFT/B3LYP using GAUSSIAN 98W, on an Intel Pentium IV 1.7 GHz processor with 512 MB RAM and Microsoft windows as the operating system. The HF/6-31G (d,p) basis set has been employed.

The first order hyperpolarizability (β_{ijk}) of LASP is calculated using HF/6-31G (d,p) basis set based on finite field approach. Hyperpolarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. It strongly depends on the method and basis set used. The 27 components of 3D matrix can be reduced to 10 components due to Kleinman symmetry [19]. The calculated first order hyperpolarizability of LASP is 4.8152×10^{-29} esu. The calculated first order hyperpolarizability (β) values are collected in Table 1. The theoretical calculation seems to be more helpful in the determination of particular components of β tensor than in establishing the real values of β. Domination of particular components indicates on a substantial delocalization of charges in those directions. It is noticed that in β_{xxx} (which is the principal dipole moment axis and it is parallel to the charge transfer axis) direction, the biggest values of hyperpolarizability are noticed and subsequently delocalization of electron cloud is more in that direction. The maximum β may be due to π-electron cloud movement from donor to acceptor which can make the molecule highly polarized and the intermolecular charge transfer interaction (intermolecular hydrogen bonding). The presence of intermolecular hydrogen bonding is confirmed with the FTIR analysis. The high value of calculated hyperpolarizability for the title compound is confirmed by the experimental SHG values reported earlier by us [14].

2.2. Spectral analysis

2.2.1. FTIR spectrum

The Fourier transform infrared spectrum of the title crystal was recorded in the region 400–4000 cm^{-1} by using PerkinElmer Spectrum RX1 spectrophotometer equipped with He–Ne laser source, KBr beam splitter and LiTaO$_3$ detector. The sample was prepared by pressing the organic crystal with KBr into pellet form. The experimental spectrum is shown in Fig. 1.