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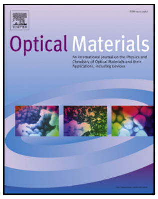

Growth, effect of protonation and hydrogen bonding interactions of L-Histidine nitrate monohydrate, a potential semi organic third order nonlinear optical material

Rejeena V. Rajan[a,b], Merin George[a], Javeesh Alex[a], D. Sajan[a,*], G. Vinitha[c]

[a] Centre for Advanced Functional Materials, Postgraduate and Research Department of Physics, Bishop Moore College, Mavelikara, Alappuzha, Kerala, 690110, India
[b] St. Cyril's College, Department of Physics, Vadakkedathukavu P.O.,Kilivayal, Adoor, Pathanamthitta, 691529, India
[c] Division of Physics, School of Advanced Sciences, Vellore Institute of Technology (VIT), Chennai, 600127, India

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ABSTRACT

Single crystal of L-Histidine Nitrate monohydrate (LHNM) has been grown from aqueous solution by evaporation technique. A comprehensive investigation of the NIR FT-Raman and FT-IR spectra was carried out with the aid of normal coordinate analysis following the scaled quantum mechanical force field methodology supported by the density functional theory (DFT) computations to analyze the effects of intramolecular charge transfer on the geometries and the vibrational modes contributing to the linear electro-optic effect of the organic NLO material. Effect of protonation and hydrogen bonding interactions has been analyzed using structural analysis, natural bond orbital analysis, and spectral analysis. The HOMO-LUMO energy gap value suggests the possibility of charge transfer within the molecule. Hyperconjugative interactions responsible for second hyperpolarizabilities have been described by NBO and AIM analyses. Hirshfeld surface analysis reveals that the van der Waals H···H (32.3%) contact plays a significant role in crystal packing and that a variety of N—H···O intermolecular contacts and hydrogen bonds leads to the formation of intermolecular charge transfer occurring in LHNM. The nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and third-order nonlinear susceptibility (χ^3) of LHNM have been determined by Z-scan technique, which points to its potential application in the field of optical limiting. The calculated value of laser damage threshold was 2.04 GW/cm^2.

1. Introduction

In recent years, there has been much effort to design and synthesize highly efficient semi organic nonlinear optical (NLO) materials, because of their large second or third order hyperpolarizablities compared to those of organic and inorganic NLO materials [1–3]. Many investigations are being done to synthesize new semi organic materials with large second-order optical nonlinearities [4] owing to their innumerable potential applications including laser technology, telecommunications, optical computing, optical data storage, etc. [5,6]. Complexes of amino acids with inorganic salts have been of interest as materials for optical second harmonic generation (SHG) due to the fact that almost all amino acids contain an asymmetric carbon atom and crystallize in non-centrosymmetric space groups [7]. Due to the presence of the planar imidazole ring in the structure, L-histidine molecules show large nonlinear optical efficiency. In recent years, many L-Histidine complexes such as L-Histidine malonate [8], L-Histidinium dihydrogen phosphate orthophosphoric acid [9], L-Histidine hydrochloride [10], L-Histidine tetrafluroborate [11], L-Histidinium bromide [12], L-Histidine hydrofluoride dihydrate [13], L-Histidine nitrate [14], L-Histidinium perchlorate [15] and L-Histidine oxalate [16,17] with good NLO efficiency have been synthesized and their single crystals have been grown and characterized. Growth, optical and dielectric properties of L-Histidine nitrate single crystal was studied by many researchers [18–20]. However, detailed vibrational analysis and third order nonlinearity studies of L-Histidine nitrate monohydrate has not been reported in literature. The present work deals with the vibrational spectral studies aided by density functional theoretical (DFT) calculations to elucidate the correlation between the molecular structure and NLO property by investigating the ICT interaction, hydrogen bonds, static, dynamic first and second hyperpolarizabilities of the third order nonlinear optical material L-Histidine nitrate monohydrate (LHNM).

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[*] Corresponding author.
E-mail address: drsajanbmc@gmail.com (D. Sajan).

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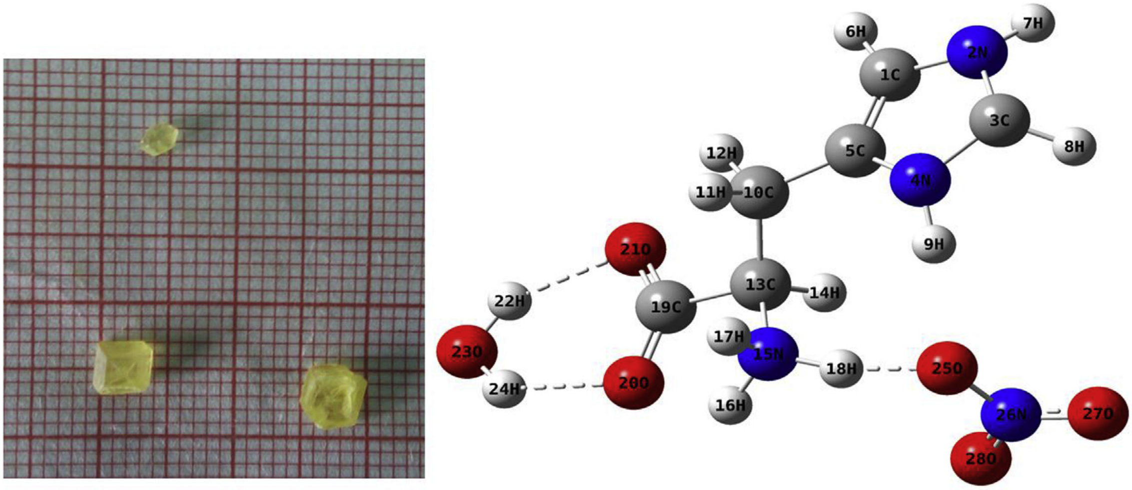

(a)

(b)

Fig. 1. (a) Photograph of the grown LHNM single crystal and 1(b) Optimized molecular structure of LHNM.

2. Experimental details

2.1. Synthesis and crystal growth

Single crystals of L-Histidine nitrate monohydrate (LHNM) were grown by slow evaporation method from commercially available L-Histidine (Sigma-Aldrich, AR grade) and Nitric acid (Sigma-Aldrich, AR grade) in equimolar ratio, dissolved in distilled water. A supersaturated solution was prepared and stirred for 2–3 h. Repeated recrystallization process was employed so as to improve the purity of the solution. Optically clear, defect-free and well-shaped good quality crystal was chosen and suspended in the mother solution, which was allowed to evaporate at room temperature for one week. Large sized single crystals were obtained due to collection of monomers at the seed crystal sites from the mother solution. Transparent crystals of size $4.0 \times 4.0 \times 3.0\,\text{mm}^3$ were obtained in a period of four weeks. Photograph of the grown crystal is shown in Fig. 1(a).

2.2. Characterization techniques

Unit cell parameters of the grown LHNM crystal were obtained using a Bruker AXS Kappa APEX II CCD Diffractometer equipped with graphite monochromatic MoKα radiation ($\lambda = 0.710$ Å). The cell data were obtained from the least-squares refinement of the setting angles of 25 reflections. ^{1}H NMR and ^{13}C NMR spectral analyses of the sample were carried out in the deuterated solvent of water using Bruker Avance III, 400 MHz NMR spectrometer. FT-IR spectrum of the sample was recorded using the Thermo Nicolet, Avatar 370 FT-IR spectrometer in the scan range 4000–450 cm^{-1} with a resolution of 2 cm^{-1}. FT-Raman spectrum was recorded using BRUKER RFS 27: Stand alone FT-Raman Spectrometer with a liquid nitrogen-cooled Ge-diode detector using Nd: YAG laser at 1064 nm of 300 mw output as the excitation source with the powder sample in a capillary tube. Thousand scans were accumulated with a total registration time of about 30 min. The spectral resolution after apodization was 2 cm^{-1}. A correction according to the fourth-power scattering factor was performed, but no instrumental correction was made. The upper limit for the wave numbers was 3500 cm^{-1}owing to the detector sensitivity and the lower limit was around 50 cm^{-1} owing to the Rayleigh line cut-off by the notch filter. UV–Vis–NIR absorption spectral data of the sample in water solution was measured using JASCO V-760 Spectrophotometer in the region 190–1100 nm.

Second harmonic generation (SHG) efficiency was measured by Kurtz and Perry powder technique [21] using Q-switched Nd:YAG laser (1064 nm) as an optical source. Finely crushed powder samples with uniform particle size of 125–150 μm were filled in a capillary tube of about 1.5 mm diameter. The input energy was measured to be 6 mJ/pulse using the power meter. Laser with a wavelength of 1064 nm, pulse width of 8 ns and repetition rate of 10 Hz was made to focus on the sample. Emission of green light (532 nm) generated from the sample was detected by the photomultiplier tube and the signal was converted into electrical signal and finally displayed on the storage oscilloscope. Z-scan technique [22] was employed to measure the nonlinear refractive index n_2 and nonlinear absorption coefficient β. Third order optical nonlinearity measurement of the sample was carried out using a 50 mW diode pumped Nd: YAG continuous wave laser **beam of** radius **$(\omega_{L)}$ 0.16 mm** and wavelength 532 nm which was focused by a lens with 3.5 cm focal length. The beam waist ω_0 at the focus was measured as 15.84 mm and the Rayleigh length as 1.48 mm. A 1 mm wide optical cell containing the solution of the sample is translated across the focal region along the axial direction. The experimental set-up for the demonstration of optical limiting under cw illumination is very similar to the Z-scan geometry.

3. Theory and computational methods

In nonlinear optics, the polarization of a compound induced by an external radiation field is often approximated as a creation of an induced dipole moment by an external electric field. The finite-field (FF) approach is a standard technique for the investigation of NLO response of a molecule because it can be used in conjunction with various electronic-structure methods to compute NLO coefficients [23]. When a system is in a weak and static electric field, its energy can be written as

$$E = E_0 - \sum_i \mu_i F^i - \frac{1}{2}\sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6}\sum_{ijk} \beta_{ijk} F^i F^j F^k - \frac{1}{24}\sum_{ijkl} \gamma_{ijkl} F^i F^j F^k F^l + \ldots\ldots$$

where E_0 is the energy of the unperturbed molecules, F^i is the field at the origin μ_i, α_{ij}, β_{ijk} and$\gamma_{ijkl}$are the components of dipole moment, polarizability, first and second hyperpolarizability tensors respectively, which are the origins of the macroscopic second- and third-order NLO susceptibilities. Microscopically, β is a third-rank tensor that contains nonvanishing elements only for a non-centrosymmetric structure, while the third-order NLO effects are described by the γ tensor. The average