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Vibrational spectroscopic and quantum chemical investigations on L-Arginine Perchlorate single crystal

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Abstract: Good quality non linear optical (NLO) crystals of L-Arginine Perchlorate (LArPCl) were grown by slow evaporation solution growth method. The grown crystals were confirmed by powder XRD studies. The vibrationfrequencies of the crystal were investigated by FT-IR spectrum. The crystal has wide range of transparency in visible region as investigated by UV–Vis-NIR spectrum. The HOMO–LUMO analysis of the title compound was theoretically investigated by DFT method.
Keywords:- NLO, FTIR, LArPCl, HOMO-LUMO.

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 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.

Materials with high nonlinear optical (NLO) activity are very useful as electro-optic switching elements and for optical information processing. The field of NLO organic molecules is dominated by donor acceptor substituted asymmetric linear molecules [1-4]. Vibrational spectral studies of the molecules can provide deeper knowledge about the relationships between molecular architecture, non-linear response, hyperpolarizability and the discovery of new efficient materials for technological applications. However, for a new synthesized molecule, it is difficult to describe its original and intricate vibrational spectral property. Density functional theoretical (DFT) methods can efficiently provide the molecular structure information, such as the vibrational assignment, the distribution of the atom charge, the polarizability and the virtual orbital energies. Recently, vibrational spectra combined with DFT calculations have been used as an effective tool in the study of NLO active compounds.

Synthesis

LArPCl was synthesized from high purity L-arginine (Merck-99 %) and perchloric acid (Merck-70 %) taken in equimolar ratio. The stoichiometric amounts of the reactants were thoroughly dissolved in deionized water. The reaction involved in the synthesis is as follows:

$NH_2\,CNHNH\,(CH_2)_3\,CH\,NH_2COOH + HClO_4 \longrightarrow NH_2\,CNH_2^{+}\,NH\,(CH_2)_3\,CHNH_3^{+}COO^{-}.\,ClO_4^{-}$

The synthesized material was then purified from aqueous solution by recrystallization process. The solubility of LArPCl was measured for various temperatures in the range of 30°C to 50°C. The temperature dependence of solubility of LArPCl in the solvent of deoinized water is shown in Fig 1. Transparent single crystals were obtained from the growth solution after 30 days. The photograph of as grown LArPCl is shown in Fig 2.

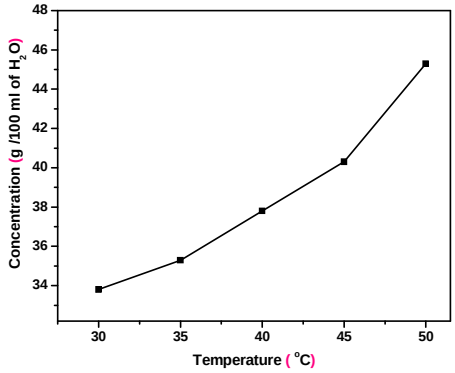

Fig 1. Solubility of LArPCl

Fig 2. Photograph of LArPCl

Results and Discussion

Powder X ray Diffraction

The sample was scanned over the range 10 - 40° at the rate of one degree/minute (Fig 3). The crystal belongs to orthorhombic system with $P2_12_12_1$ space group. The lattice parameters are a = 5.0840 Å, b = 13.8296 Å and c = 16.5681 Å.

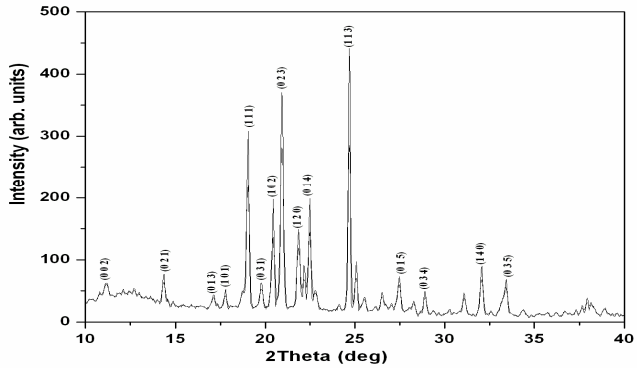

Figure 3. Powder XRD pattern of LArPCl

FT-IR spectrum

The infrared spectrum of LArPCl recorded in the range 4000 – 500 cm^{-1}using the Bruker IFS 66V FT-IR spectrometer by potassium bromide pellet technique to confirm the presence of functional groups are shown in Fig 4. It is noted from the spectrum that the bands at 3476 and 3403 cm^{-1} evidence the presence of weakly hydrogen bonded N-H groups. The bands at 3062, 2973 2946, 2881, and 2830 cm^{-1} relate to stretching vibrations of C-H bonds of CH and CH_2 groups. The intense band comprising of peaks near 1636 cm^{-1} may be assigned to asymmetric stretching of COO^{-}, asymmetic bending of NH^{3+} and NH_2 bending vibrations. The symmetric bending vibrations of NH_3 + and COOH groups are positioned at 1490 and 1423 cm^{-1}.

Optical transmittance and nonlinear optical studies

The optical transmission spectrum of LArPCl single crystal was recorded in the wavelength region of 200-1800 nm using VARIAN CARY 5E spectrometer. The spectrum of LArPCl crystal is shown in Figure 5. It

is evident that the crystal possesses a wide optical transparency window from 290 -1100 nm. It is also clearly indicates that the UV cut-off wavelength lies at 290 nm. The presence of low cut-off wavelength and the wide optical transmission window are the suitable parameters for frequency doubling of laser radiation.

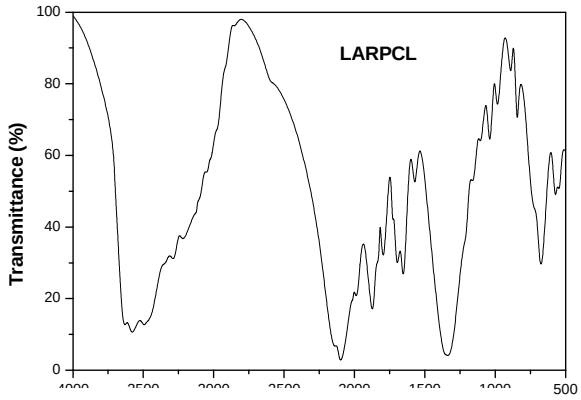

Fig 4. FT-IR spectrum of LArPCl

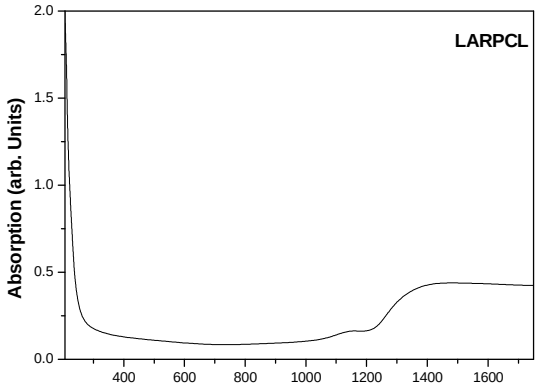

Fig 5. UV- Vis NIR spectrum of LArPCl

HOMO-LUMO Gap:

The HOMO-LUMO energy gap of LArPCl, reveals that the energy gap reflects the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron, HOMO represents the ability to donate an electron. Moreover the lower value in the HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule [5]. The HOMO-LUMO energy gap of LArPCl was calculated using B3LYPbasis set and the HOMO-LUMO gap value of the studied compound is -0.15856 a.u

Conclusion

Single crystals of LArPCl were grown by slow evaporation technique at room temperature. The grown crystal was confirmed by Powder XRD. Spectral assignments are carried out for various vibrational frequencies. Molecular energy gap of LArPClwas found to be -0.15856 a.uby HOMO-LUMO analysis. The optical studies reveal that the crystal has very low absorption in the entire visible and infrared region, with the lower UV cut off around 290 nm, which is an essential consideration for NLO crystals.

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