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Vibrational Spectral Investigation of Nonlinear Optical L-Asparagine–L-Tartaric Acid : A Combination of Experimental and Theoretical Study

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Abstract : L-Asparagine–L-Tartaric (LAsT) acid a second order nonlinear optical (NLO) material was studied in-depth by using vibrational spectra and density functional theory (DFT). The Fourier transform infrared (FT-IR) spectrum was recorded in the range 4500 – 500 cm^{1}. Meanwhile, the DFT computations are performed at B3LYP/6-31G (d, p) level to derive equilibrium geometry, vibrational wavenumbers and first hyperpolarizability, and the scaled theoretical wavenumbers are also shown to be in good agreement with experimental data. The nonlinear characteristic and thermal stability of the crystal were also investigated.

Key Words : L - Asparagine - L - Tartaric, Density functional theory, Fourier transform infrared spectroscopy, Nonlinear optical.

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1. Introduction

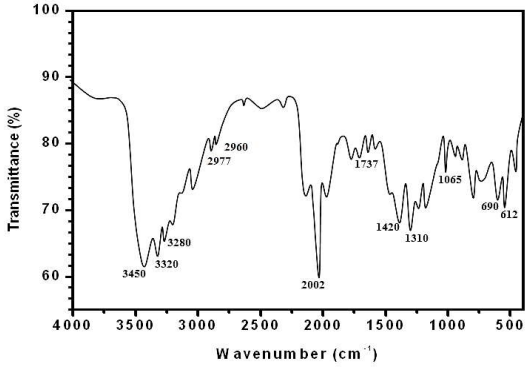
Density functional theory (DFT) calculations have provided excellent agreement with experimental vibrational frequencies of organic compounds, if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation; basis set limitations and anharmonicity [1-3]. Due to their high molecular hyperpolarizabilities, organic materials display a number of significant nonlinear optical properties. Last decade NLO materials are

extensively researched quantum mechanically to obtain an optimized molecular structure. Nonlinearity in organic chromophores can be synthetically modulated by varying the composition or length of conjugated p-systems, and by evaluating the effects of various electron-donor and electron-acceptor groups. The grown crystals were then characterized by single crystal X-ray diffraction analysis, DFT analyses, first order hyperpolarizability studies [4] and second harmonic generation efficiency measurements.

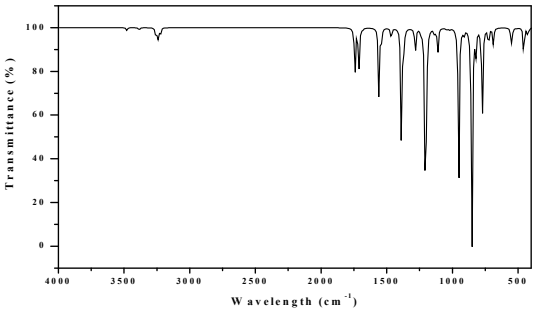
2. Vibrational Spectral Analysis

The best of our knowledge no theoretical vibration studies were made on the title compound. The title compound consists of 33 normal modes of vibrations which in turn confirm the nonlinearity of the molecule. In the case of non linear molecule there are three degrees of rotation as the rotation about all the three axes (x,y,z) will result in a change in the position of the atoms. So, for a non linear molecule of n-atoms, the vibrational degrees of freedom can be calculated as 3n-6. where n - number of atoms.

FT-IR transmission spectrum of LAsT in the region 4000-400 cm^{-1}. It is evident from the spectrum that, there is a broad band between 3800 and 2700cm^{1}. It includes OH stretch of water at 3450 cm^{-1} and N-H vibration at 3320 and 3280 cm^{-1}. The characteristic CH vibrations of tartaric acid produce peaks at 2977 and 2960 cm^{-1}. In the overtone region, there is a prominent band near 2002 cm^{-1} due to combination of the asymmetrical NH_3^+ bending vibration and the torsional oscillation of the NH_3^+ groups. The C=O stretch of tartaric acid gives a peak at 1737 cm^{-1}. The asymmetric and symmetric COO vibrations produce peaks at 1553 and 1420cm^{-1}. The C-O stretching and OH deformation produce peak at 1310 cm^{-1}. The alcoholic C-O stretch gives its peak at 1065 cm^{1}. From the spectroscopic investigation, the presence of all the fundamental functional groups of the grown sample is confirmed qualitatively. From the IR spectral analysis the presence of water is evident in the lattice of L-Asparagine.



FT-IR spectrum of LAsT



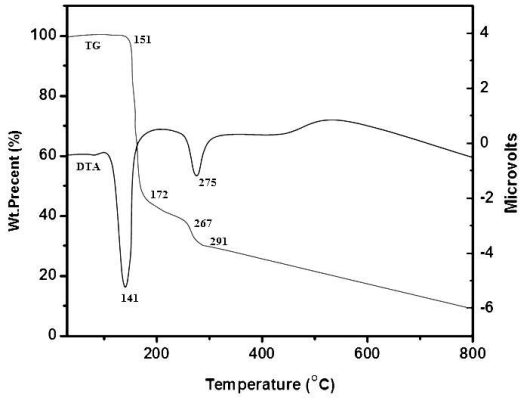
Simulated FTIR spectrum of LAsT

3. Geometric and Hyperpolarizability Calculations :

The optimized structure of LAsT was calculated by DFT (B3LYP) with basis set 6-31G (d, P). Theoretical calculation provides another method to investigate substantial characters of materials. As hyperpolarizability is difficult to measure directly, computational calculation is an alternate choice. The first order hyperpolarizability β_o of title molecular system and related properties (β_o, α_o, $\Delta\alpha$) of LAsT are calculated using 6-31G(d, p) basis set, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First order hyperpolarizability is a third rank tensor that can be described by a 3x3x3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry**.** It can be given in the lower tetrahedral format. It is obvious that the lower part of 3x3x3 matrices is a tetrahedral.The first-order hyperpolarizibility (β_{ijk}) of the novel molecular system of LAsT was calculated. Hyperpolarizibility is a third rank tensor and strongly depends on the method and basis set used [5].

4. Thermal analysis

The two broad endothermic peaks at 141 and 275 °C represent the decomposition of molecular fragments in two stages. This weight loss is followed by a major weight loss pattern between 172 and 267 °C occurring in two stages, the total weight loss of these stages correspond to 20 % of the substance due to release of CO_2 and CO molecules in tartaric acid. The reactions of simplest amino acids induced by heating include the condensation reactions of carboxyl and amino groups leading to the formation of peptide bonds. The total weight loss nearly equals to 90% and the resulting residue(10 %) is stable upto 800 °C. From this study it is concluded that the melting and decomposition occur in successive steps but the process appear to occur closely. This analysis indicates the possible NLO application of the material up to 141 °C.



TGA and DTA curves of LAsT

5. Conclusion

Single Crystal of L-Asparagine–L-Tartaric acid (LAsT) is conveniently grown by slow evaporation technique at room temperature. Optimized structure of the isolated LAsT molecule was confirmed to be minimum energy. First order hyper polarizability of LAsT is calculated and presented. The sample is thermally stable up to 141 °C.

References

[1] Madhavan. J, Aruna. S, Anuradha. A, Premanand. D, Vetha Potheher. I, Thamizharasan. K, Sagayaraj. P, *Optical Materials*, 2007 , 29, 1211-1216

[2] D. Sankar , P. Praveen Kumar , J. Madhavan *Physica B* , February 2010, 1233–1238

[3] Ramesh Kumar G., Gokul Raj S., Mohan R. and Jayavel R., (2005), Crystal Growth & Design, Vol.6, 1308-1310.

[4] Praveen Kumar P , V. Manivannan , S. Tamilselvan , S. Senthil ,M. Victor Antony Raj ,Sagayaraj P , J. Madhavan, Optics Communications , May 2008.

[5] Kleinman. D. A, *Phys. Rev*. 1977, 126, 1962.