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Multi-photon absorption effect and intra-molecular charge transfer of donor-π-acceptor chromophore ethyl p-amino benzoate

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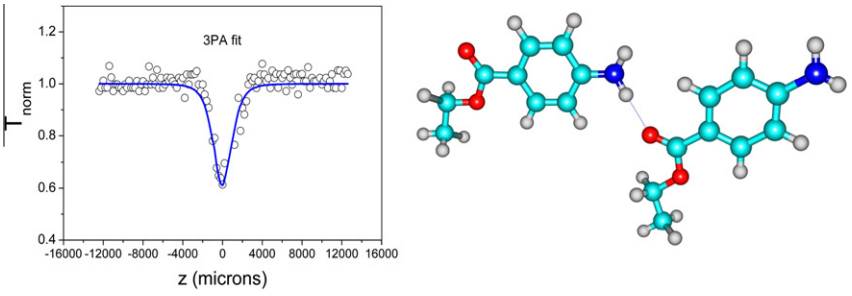
HIGHLIGHTS

- Ethyl p-amino benzoate single crystal was grown by slow evaporation solution growth method.
- FT-Raman and infrared spectra of the nonlinear optical material ethyl p-amino benzoate have been recorded and analyzed.
- The hydrogen bonding and the possible interactions were also calculated by using NBO analysis.
- Nonlinear optical absorption of the sample has been studied by open-aperture *z*-scan technique.

GRAPHICAL ABSTRACT



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ABSTRACT

Fourier transform (FT)-Raman and infrared (IR) spectra of the nonlinear optical (NLO) material ethyl p-amino benzoate (EPAB) have been recorded and analyzed. The geometry and harmonic vibrational wavenumbers are calculated with the help of B3LYP density functional theory method. The detailed interpretation of the vibrational spectra has been carried out with the aid of normal coordinate analysis following the scaled quantum mechanical force field methodology. Stability of the molecule arising from hyperconjugative interactions leading to its NLO activity and charge delocalization have been analyzed using natural bond orbital (NBO) analysis. Employing the open-aperture *z*-scan technique, NLO absorption of the sample has been studied in two excitation regimes, using 100 fs and 5 ns laser pulses respectively. It is found that EPAB is a three-photon absorber for 100 fs pulses at the excitation wavelength of 800 nm. For ns pulses at 532 nm it exhibits strong optical limiting, indicating possible photonics applications.

Introduction

In recent years there has been considerable interest in the development of organic molecular crystals with spectral properties suitable for nonlinear optics, as well as their application in optical devices for information processing [1]. Organic materials with delocalized π electrons have many advantages such as architectural flexibility, ease of fabrication, ultrafast optical response, and larger nonlinearity [2]. Donor–acceptor (D–A) molecular crystals and materials have recently attracted considerable academic and technological research attention for their applications in nonlinear optics [3]. Understanding the structure–function relationships that relate specifically to organic molecular materials could lead to new design concepts for producing benign, high-performance, novel molecular materials. Organic chemistry provides a number of

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advantages in the development molecular materials design and synthesis. Usually, designing proper D or A building blocks over a wide range of different functional units could rationally control nonlinear properties of the D–A materials. Moreover, their nonlinear properties could also be adjusted by appropriate manipulation of their chemical structures such as different connectors linking the D/A building blocks, distance between the D/A units, and the symmetry of the molecule [4,5].

Interest in the development of materials exhibiting large multiphoton absorption has increased in the last decade, motivated by their potential application in optoelectronics. Two-photon absorption (TPA) is the basis for an increasing number of optical and electro-optical applications that include data storage [6,7], three-dimensional micro-fabrication [8,9], biological imaging [10–12], optical limiting [13–16], and photodynamic therapy [17,18]. The potential of these technologies, in turn, continues to drive development of materials with improved TPA properties. For example, TPA enhanced materials boost absorption efficiency at low excitation intensity and, therefore, help minimize damage due to laser irradiation. Therefore, an improved understanding of chromophoric structural factors that may be manipulated to improve TPA will undoubtedly impact a variety of technologies which depend on this NLO effect. EPAB also known as benzocaine is one of the benzoic acid derivatives mainly used as a best local anaesthesia. Studies on the structural, thermal and optical properties of ethyl p-amino benzoate single crystal and the difficulties involved in the growth of EPAB have been reported [19–21]. Vibrational spectral studies for the benzoate derivatives also are available in literature [22].

The present work focuses on the vibrational spectral study of the push–pull organic NLO material ethyl p-amino benzoate (Fig. 1) to elucidate the correlation between its molecular structure, NLO property and charge transfer, supported by the scaled quantum mechanical (SQM) force field technique based on DFT calculations. In addition, the absorptive nonlinearity of EPAB is studied by the open aperture *z*-scan technique in both the femto second and nanosecond pulse excitation regimes, employing 100 fs and 5 ns laser pulses respectively.

Experimental

Preparation

The commercially available organic NLO material of ethyl p-amino benzoate (CDH make) was purchased and its purity was further improved by recrystallization processes using Xylene as the solvent. Then the dissolved solution was filtered and kept in a oven for dryness. The dried salt was used as the raw material for preparing the concentrated solution of the title compound. In the present growth experiment, we have used the mixed solvents of Xylene with less than 1M concentration of dimethyl sulfoxide (DMSO). The filtered solution was housed in the constant temperature bath (CTB) with the setting temperature of 31 °C. After a span of 16 days, good quality single crystals have been harvested from the mother solution. The grown single crystal is shown in Fig. 2.

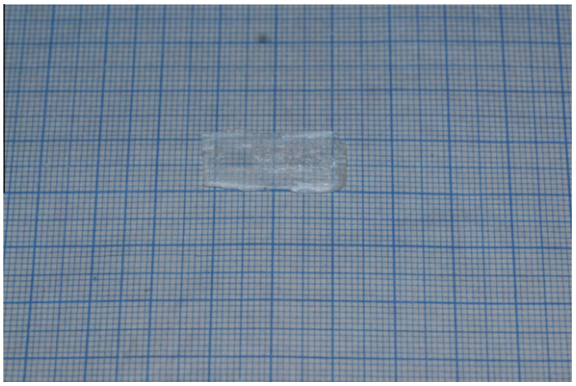

Fig. 2. As grown single crystal of EPAB.

IR and Raman and UV measurements

FT-IR spectrum of the synthesized material was recorded in the wavenumber range 400–4000 cm^{-1} by KBr pellet technique (Thermo Nicolet AVATAR 370 DTGS FT-IR spectrophotometer). The NIR-FT-Raman spectrum of NBG using 1064 nm excitation was recorded in the region 10–4000 cm^{-1} using BRUKER RFS 100/s FT-Raman Spectrometer using powder sample taken in a capillary tube and the Raman spectrum was recorded with an Nd:YAG laser at 1064 nm with an output of 300mW used as the excitation source and with a liquid nitrogen cooled Ge-diode detector; 1000 scans were accumulated with a total registration time of about 30 min. The spectral resolution after apodization was 2 cm^{-1}. The UV–Vis absorption spectrum of the sample was recorded in Xylene solution using a Shimadzu UV–Vis spectrophotometer in the spectral region of 200–400 nm.

Nonlinear optical studies – z-scan measurement

Open-aperture *z*-scan measurements were performed to determine the nonlinear transmission of laser light through the samples. The *z*-scan is a widely used technique developed by Sheik-Bahae

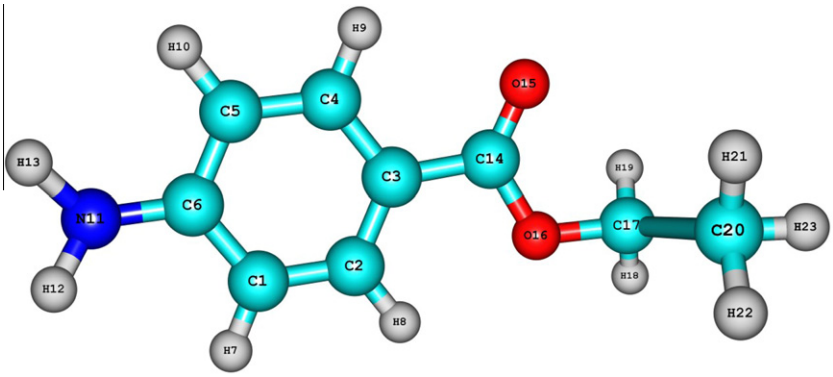

Fig. 1. Optimized structure of EPAB monomer calculated at B3LYP/6-311++G (d,p).