

Structural and electronic contributions to hyperpolarizability in methyl *p*-hydroxy benzoate

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Abstract

The single crystals of methyl *p*-hydroxy benzoate (MPHB) are grown from methanol solution by a low temperature solution growth technique. The SHG efficiency is tested using Q-switched Nd:YAG laser of wavelength λ at 1064 nm, which is approximately 1.2 times that of urea. Vibrational spectral analysis using NIR-FT Raman and FT-IR spectra is carried out to understand the structural and electronic contributions to hyperpolarizability in MPHB. The DFT computations are also performed at B3LYP/6-311G(d,p) level to derive equilibrium geometry, vibrational wavenumbers and intensities. The results of ab initio calculations at HF/6-311G(d,p) level show that the vibrational contribution for the second-order electro-optic coefficient in MPHB is about 19.5%. Vibrational spectral studies also provide evidence for the charge transfer interaction between the donors and the acceptor group through the π -system. The π -electron cloud movement from donor to acceptor can make the molecule highly polarized and the intramolecular charge transfer interaction must be responsible for the nonlinear optical properties of MPHB. The splitting of the carbonyl mode may be attributed to the intramolecular association based on C=O \cdots H type hydrogen bonding in the molecule. The conjugation and influence of intermolecular hydrogen bonding (C=O \cdots H) type network in the crystal results in lowered C=O stretching wavenumber.

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1. Introduction

Nonlinear optics (NLO) is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in areas such as telecommunications, signal processing, and optical interconnections [1–3]. Organic materials have been of particular interest because the nonlinear optical response in this broad class of materials is microscopic in origin, offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials [4–6]. Also, organic nonlinear optical materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultrafast response times, and high optical thresholds for laser power as compared with inorganic materials. Organic molecules with significant nonlinear optical

activity generally consist 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 [7]. 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 [8,9]. Due to their potential applications in photonic devices, the nonlinear optical properties of molecules, and their hyperpolarizabilities have become an area of extensive research, and lot of experimental [10,11] and theoretical efforts [12,13] are focused on bulk NLO properties as well as their dependence on the first hyperpolarizabilities of molecules. Vibrational spectral studies of the molecules can provide deeper knowledge about the relationships between molecular architecture, nonlinear response, and hyperpolarizability and support the efforts towards discovery of new efficient materials for technological

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applications. NIR-FT Raman spectroscopy combined with quantum chemical computations have recently been used as effective tools in the vibrational analysis of drug molecules [14], biological compounds [15], natural products [16,17] and NLO active compounds [18], since fluorescence free Raman spectra and computed results can help unambiguous identification of vibrational modes as well as the bonding and structural features of complex organic molecular systems. The present work is a vibrational spectral study on the relationships between molecular structural features, nonlinear response and hyperpolarizability of methyl *p*-hydroxy benzoate (MPHB) with special emphasis on the role of intramolecular charge transfer (ICT) mechanism in such organic NLO materials.

2. Experimental

2.1. Preparation

The single crystals of methyl *p*-hydroxy benzoate (MPHB) were grown in a methanol solution by low temperature solution growth technique [19]. Colourless transparent crystals of title compound were obtained within 2 weeks. Repeated recrystallisation yielded good quality crystals. The single crystals of maximum size of around 0.6 mm were obtained.

2.2. IR and Raman measurements

The IR spectrum (Fig. 1) of MPHB was recorded using Perkin-Elmer Spectrum One FT-IR spectrometer in the region 450–4000 cm^{-1} with the sample in standard KBr pellet technique with 1 mg sample per 300 mg KBr was used. The spectral resolution was 2 cm^{-1} . The NIR-FT Raman spectrum (Fig. 2) was obtained on a IFS 66v BRUKER spectrophotometer with the powder sample taken in a capillary tube and the Raman spectra were recorded using Nd:YAG laser excitation of wavelength 1064 nm with 300 mW output and liquid nitrogen cooled Ge-diode detector. About 1000 scans were accumulated with a total registration time of about 30 min. The spectral resolution after apodization was 4 cm^{-1} . A correction according to the fourth power scattering factor was performed, but no correction to instrumental was done.

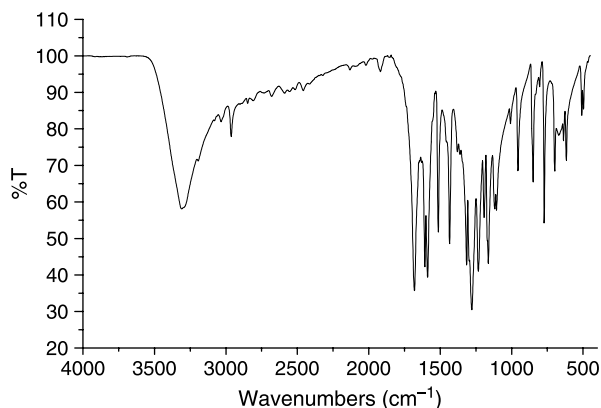


Fig. 1. FT-IR spectrum of MPHB.

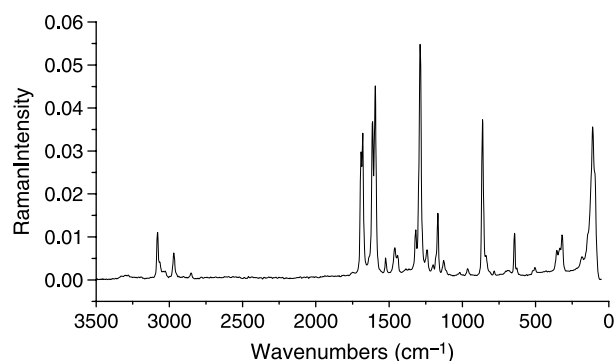


Fig. 2. NIR-FT Raman spectrum of MPHB.

The upper limit for the Raman shift is 3500 cm^{-1} due to the detector sensitivity and the lower Raman shift is around 10 cm^{-1} due to the Rayleigh line cut off by a notch filter.

2.3. Second harmonic generation efficiency measurements

The NLO SHG efficiency of MPHB (particle size 100–200 μm) is measured by the Kurtz-Perry powder SHG method [20] using Q-switched Nd:YAG laser of 1064 nm wavelength. The input laser beam was passed through the sample after reflection from an IR reflector. The output from the sample was filtered by an IR filter to eliminate the fundamental and the second harmonic was detected using monochromator and PMT. The second harmonic generation efficiency of MPHB was evaluated to be 1.2 times that of urea.

2.4. Crystal structure

MPHB crystallizes in space group *Cc*. From the single crystal XRD data [19], it is observed that the crystal belongs to monoclinic system with the following cell dimensions: $a = 13.977(1) \text{ \AA}$, $b = 15.774(1) \text{ \AA}$, $c = 12.684(1) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 131.97^\circ$. The stability of the molecular conformations is reached with a balance between intermolecular hydrogen bonds of the hydroxyl groups with carbonyl oxygen ($\text{C}=\text{O} \cdots \text{H}$). In both the intermolecular H-bonds, one hydroxyl oxygen atom acts as a donor to the adjacent carbonyl oxygen.

2.5. Origin of nonlinear effects

Nonlinear optical effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields. When a beam of light is impinged on to a material, it causes the charges of the atoms to oscillate. In the linear regime the amount of charge displacement is proportional to the instantaneous magnitude of the electric field. The charges oscillate at the same frequency as the frequency of the incident light. The oscillating charges either radiate light at that frequency or the energy is transferred into nonradiative modes that result in material heating or other energy transfer mechanisms. With small fields, the displacement of charge from the equilibrium position, polarization

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