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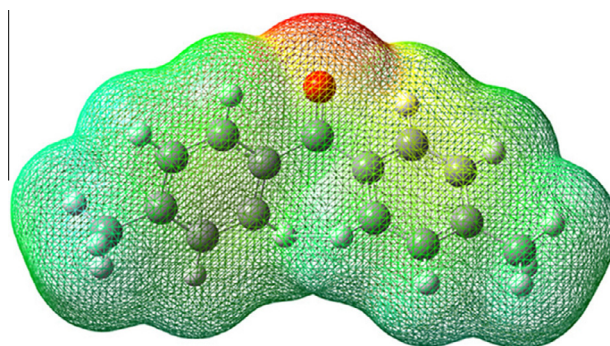
Normal coordinate analysis and Nonlinear Optical Response of cross-conjugated system 4,4-Dimethyl Benzophenone

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HIGHLIGHTS

- DFT calculations have been performed on the NLO crystal 4,4-Dimethyl Benzophenone (4DMBP).
- The NCA was performed on 4DMBP to reproduce its experimental harmonic vibrational wavenumbers excellently.
- The IR and Raman spectra of the compound were analyzed.
- The calculated first order hyperpolarizability of 4DMBP calculated and is found to be 1.97×10^{-30} e.s.u.
- NBO, HOMO and LUMO analysis were also performed by DFT approach.

GRAPHICAL ABSTRACT



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ABSTRACT

FT-Raman and IR spectra of the nonlinear optical active crystal, 4,4-Dimethyl Benzophenone (4DMBP) have been recorded and analyzed. The equilibrium geometry, harmonic vibrational wavenumbers of 4DMBP investigated with the help of density functional theory (DFT) method. The assignments of the vibrational spectra have been carried out with the help of normal coordinate analysis (NCA) following the scaled quantum mechanical force field methodology (SQMFF). The calculated hyperpolarizability value shows the nonlinear optical activity of the molecule. The value of HOMO–LUMO energy, Mulliken and the natural charges are calculated and analyzed. The Natural bond orbital analysis confirms the occurrence of intramolecular charge transfer interaction.

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Introduction

Organic materials with delocalised π electrons have attracted considerable research attention as nonlinear optical (NLO) materials in recent years with respect to their future potential applications in the field of optoelectronics and photonics, due to their large first hyperpolarizabilities β [1–4]. In order to improve the second-order NLO response at the macroscopic level, one must improve the NLO response at the molecular level [5]. Extensive literature is available

on the organic NLO materials with deep theoretical and experimental studies [6–10]. The NLO efficiency can be enhanced by increasing the extent of charge transfer across the molecule by placing a strong electron donor and acceptor groups at the ends of the highly polarizable conjugated bridge. At the molecular level the hyperpolarizabilities β and γ are responsible for the nonlinear optical properties including second and third harmonic generation and electro-optic effect. Experimental measurements and theoretical calculations on molecular first hyperpolarizability β become one of the key factors in the second-order NLO materials design. Theoretical determination of hyperpolarizability is quite useful both in understanding the relationship between the molecular

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structures and nonlinear optical properties, which providing a guideline to experimentalists for the design and synthesis of organic NLO materials [11]. Benzophenone derivatives were interesting organic NLO materials that show high SHG conversion efficiency compare to KDP [12]. In Benzophenone derivative molecules the carbonyl group presents at the middle was split the conjugated system into relatively two independent parts. Therefore, Benzophenone derivatives can be regarded as cross-conjugated molecules that possess two independent hyperpolarizable parts with a two-dimensional character. By placing an electron group on each phenyl ring one can substantially enhance the NLO efficiency of Benzophenone derivative molecules. The substitution of weak electron donors such as Cl, Br, F, N(CH₃)₂, CH₃ and OH groups on phenyl group results in noncentrosymmetric structures and have been suggested as the best electron donor groups for designing NLO chromophores. Therefore, Benzophenone derivatives have been very much useful due to their high nonlinearity as well as their transparency, and the cross-conjugated path in these molecular systems appears as a powerful electronic system for the molecular engineering of efficient NLO materials.

Quantum chemical computations are excellent methods in the design of NLO molecules and help to predict some properties of the new materials, such as molecular dipole moments, polarizabilities and hyperpolarizabilities [13–17]. Vibrational spectra with the help of quantum chemical computational methods have been proved to be an essential tool for predicting various molecular properties such as hydrogen bonding, inter and intramolecular charge transfer interaction of the organic molecule [18–20]. The present work aim that to study the structure activity relationship of the molecule 4,4-Dimethyl Benzophenone using DFT computation and vibrational spectra. The HOMO–LUMO energy gap, polarizability and hyperpolarizabilities of 4,4-Dimethyl Benzophenone are calculated to identify the NLO activity of the molecule. A systematic study of the geometrical parameters, vibrational and THz spectra of 4,4-Dimethyl Benzophenone (4DMBP) crystal have been carried out using experimental and density functional theory (DFT) computations. The natural bond orbital (NBO) analysis explains the eventual charge transfers interaction present in the molecule.

Experimental

Growth, IR, Raman and THz spectra

The compound 4,4-Dimethyl Benzophenone (4DMBP) was dissolved in xylene to get saturated aqueous solution and was allowed to evaporate slowly at 35 °C by slow evaporation technique. The small crystal of (4DMBP) was harvested after 20–30 days. The Infrared spectrum of the sample was recorded between 4000 and 400 cm⁻¹ on a Mattson 1000 FTIR spectrometer which was calibrated using polystyrene bands. The FT-Raman spectrum of the sample was recorded between 3500 and 50 cm⁻¹ regions on a Bruker FRA 106/S FT-Raman instrument using 1064 nm excitation using Nd:YAG laser. The detector is a liquid nitrogen cooled Ge detector.

The THz measurements were performed using a standard THz time domain spectrometer (TDS). The THz beam is generated from antenna structure put over low temperature grown GaAs by gating it with 10 fs pulses (repetition rate 76 MHz) having 780 nm centre wavelength. The generated THz pulses were transmitted through a standard aperture and the pulse waveform. A grown crystal of size 2 mm is placed in the THz optical path and the waveforms are recorded. The numerical Fourier transforms of the pulses were taken and the additional absorption dips due to the presence of the samples were found. All measurements have been done at room

temperature. The range of the THz for this experiment is 0.025–2.8 THz (limited by detector ZnTe).

Computational details

Gaussian 09 [21] software package was used for all the theoretical calculations. The structure of the 4DMBP molecule were optimized using the Becke–Lee–Yang–Parr hybrid exchange correlation three-parameter functional (B3LYP) with 6-31G(d) [22]. The optimized geometry corresponding to the minimum on the potential energy surface has been obtained by solving self-consistent field equation iteratively. The harmonic vibrational wavenumbers have been analytically calculated by taking the second-order derivative of energy using the similar level of theory. The determination of the internal coordinate contributions to the normal modes is of vital importance in attaining a correct assignment of the fundamental modes observed in the experimental spectra. Considering this, the mode descriptions of the calculated normal modes of 4DMBP is given with respect to the potential energy distributions (PEDs), using a SQM methodology [23,24] by employing MOLVIB program version 7.0 written by [25,26]. Multiple scaling of the force field was performed by the SQM procedure to offset the systematic errors caused by basis set incompleteness, neglect of electron correlations and vibrational anharmonicity b [27]. Force constants, depolarization ratio, IR intensities and Raman activities have also been calculated. The calculated Raman activities (*S_i*) have been converted to relative Raman intensities (*I_i*) using the following relationship derived from the basic theory of Raman scattering [28,29]

$$I_i = \frac{f(v_o - v_i)^4 S_i}{v_i \left[1 - \exp\left(\frac{-hc v_i}{kT}\right) \right]} \quad (1)$$

where *v_o* is the exciting wavenumber, *v_i* is the vibrational wavenumber of the *i*th normal mode, *h*, *c* and *k* are universal constants, and *f* is the suitably chosen common scaling factor for all the peak intensities.

Result and discussion

Geometry optimization

The optimized molecular geometry (Fig. 1) represents an isolated molecule under ideal conditions with a stationary point at the potential energy surface the convergence was confirmed by observing no imaginary vibrational wavenumbers. Table 1 shows the selected optimized parameters of 4DMBP molecular unit in solid phase using B3LYP/6-31G(d) level along with experimental value [30]. The optimized geometry shows that the calculated bond lengths are slightly longer than the experimental values. This variation is due to the fact that the optimization was performed in an isolated condition. The changes in bond length of the C–H bond on substitution are due to the electron donation group within the benzene ring which reduces the electron density of the carbon atom. The agreement for bond angles is not as good as that for

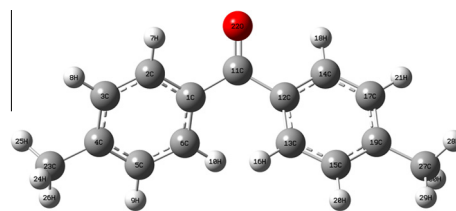


Fig. 1. Optimized structure 4DMBP calculated at DFT level.

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