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Three-photon absorption and vibrational spectroscopic study of 2-methylamino-5-chlorobenzophenone

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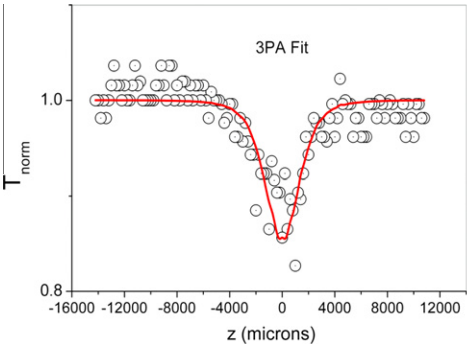
HIGHLIGHTS

- Vibrational spectra of the NLO material 2-methylamino-5-chlorobenzophenone have been analyzed.
- Nonlinear optical absorption of the sample has been studied by open-aperture Z-scan technique.
- The natural bond orbital (NBO) analysis has been carried out.
- The electronic absorption properties were studied.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, the vibrational spectral analysis and three-photon absorption properties of an organic material of 2-methylamino-5-chlorobenzophenone have been reported. 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 (SQM). SQM force fields have also been used to calculate potential energy distribution (PED) in order to make conspicuous vibrational assignments. The nonlinear absorption properties have been investigated in ethanol solution at 532 nm using the Z-scan technique employing laser pulses of 5 ns duration. Open aperture Z-scan data reveal the presence of effective three-photon absorption for ns pulses at 532 nm resulting in a strong optical limiting behavior, indicating possible photonic applications.

Introduction

Organic materials have been extensively studied for their NLO properties [1–9]. NLO effects in organic molecules originate from the delocalized π-electron system and the strong donor–acceptor intermolecular interaction, as well as from the ability to crystallize into non-centrosymmetric units. Benzophenone derivatives are an important class of NLO materials and having a broad spectrum of applications in the chemical and biochemical fields [10,11] and they are widely used in UV-screens to protect industrial products from light induced damage [12]. These different industrial applications of benzophenone derivatives have encouraged us to investigate the spectroscopic properties of benzophenone derivatives.

The acceptor/donor substituent on the aromatic rings leads to the change in structural, vibrational and NLO properties of the benzophenone. Vibrational spectra obtained through IR and Raman spectral studies of benzophenone and its derivatives have been

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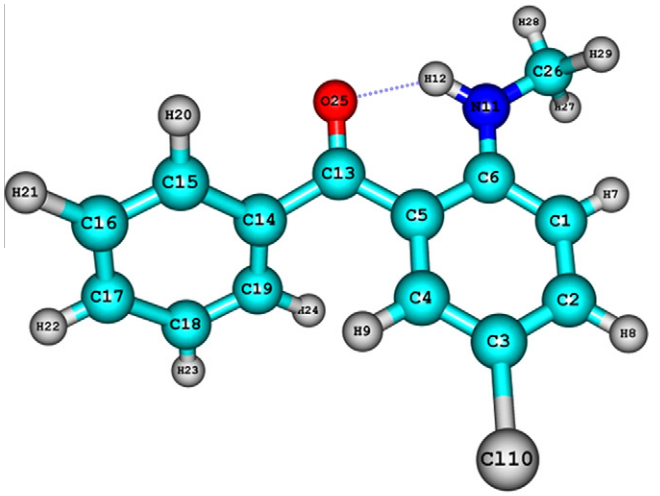

Fig. 1. Molecular structure and atomic numbering of 2-methylamino-5-chlorobenzophenone.

reported by several authors in the molten, solid, vapor, liquid and crystalline phases [13–23]. For instance, the structural [24], thermal, dielectric and optical studies of 2-methylamino-5-chlorobenzophenone (MACB) single crystal have been reported [25].

An experimental investigation of the nonlinear absorption properties of MACB, as well as its detailed vibrational spectral investigation (Fig. 1) using the scaled quantum mechanical (SQM) force field technique based on density functional theory (DFT) calculations have been reported. The experimental and theoretical results are found to support each other, and the calculations are valuable for providing a reliable insight into the vibrational spectra and molecular properties.

Experimental and computational details

Sample preparation

2-methylamino-5-chlorobenzophenone (99%) was purchased from sigma–Aldrich. Recrystallization of MACB was carried out as suggested by Cox et al. [24] by slow evaporation method using ethanol as solvent. Good transparent single crystals have been harvested from the mother solution within a weak.

Spectroscopic measurements

FT-IR spectrum of 2-methylamino-5-chlorobenzophenone 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 was recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 10–4000 cm^{-1} on a Bruker RFS 100/S spectrometer using powder sample taken in a capillary tube. The detector is a liquid nitrogen cooled Ge detector. 1000 scans were accumulated with a total registration time of about 30 min. using a laser power of 300 mW. The spectral resolution after apodization was 2 cm^{-1}. The UV–Vis absorption spectrum of the sample was recorded in ethanol using a Shimadzu UV–Vis spectrophotometer in the spectral region of 200–600 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 et al. [26] to measure the optical nonlinearity of materials, and the open aperture Z-scan gives information about the nonlinear absorption coefficient. Here a laser beam is focused using a lens and is passed through the sample. The beam's propagation direction is taken as the z-axis, and the focal point is taken as $z = 0$. The beam will have maximum energy density at the focus, which will symmetrically reduce towards either side for the positive and negative values of z. The experiment is done by placing the sample in the beam at different positions with respect to the focus (different values of z) and measuring the corresponding light transmission. The graph plotted between the sample position z and the normalized transmittance of the sample T (norm.) (Transmission normalized to the linear transmission of the sample) is known as the Z-scan curve. The nonlinear absorption coefficient of the sample can be numerically calculated from the Z-scan curve. In our experiment, ethanol solutions of the samples taken in 1 mm cuvettes were irradiated by plane polarized 5 ns laser pulses at 532 nm which is obtained from the second harmonic output of a Q-switched Nd:YAG laser (MiniLite, Continuum). The laser pulse energy was 160 μJ and the beam focal spot radius (ω_0) was 18 μm. These values yield a Rayleigh range (z_0) of 1.9 mm, and on-axis peak intensity (I_0) of 6.29×10^9 W/cm^2, for a spatially Gaussian beam. The laser was run in the single shot mode using a data acquisition program, with an approximate interval of 3–4 s between each pulse. This low repetition rate prevents sample damage and cumulative thermal effects in the medium. The sample concentration was so adjusted that the linear transmission was 60%.

Computational details

The quantum chemical calculations of MACB have been performed using the B3LYP level of theory supplemented with the Dunning's correlation consistent basis set (cc-pvTZ), using the Gaussian 09 program [27] to calculate optimized geometry and vibrational wavenumber with their IR intensities and Raman scattering activities. The optimized geometries corresponding to the minimum on the potential energy surface have been obtained by solving self-consistent field (SCF) equation iteratively. Harmonic vibrational wavenumber have been calculated using analytic second derivatives to confirm the convergence to minima on the potential surface and to evaluate the zero-point vibrational energies without imposing any molecular symmetry constraints. It is a well-known fact that ab initio calculations tend to overestimate the vibrational wavenumber with respect to the experimental ones. This is due to several reasons the use of such as finite basis set, the incomplete implementation of the electronic correlation and the neglection of anharmonicity effects in the theoretical treatment. To improve the agreement between the predicted and observed wavenumber, the computed harmonic wavenumbers are usually scaled for comparison. In this work, the force field was scaled according to the SQM procedure [28], the Cartesian representation of the force constants were transferred to a nonredundant set of local symmetry coordinates, chosen in accordance to the recommendations of Pulay et al. [29]. The scale factor calculation and characterization of the normal modes using potential energy distribution (PED) were done with the MOLVIB program 7.0 written by Sundius [30]. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a bandwidth (FWHM) of 10 cm^{-1}.

The prediction of Raman intensities were carried out by following the procedure outlined below. The Raman activities (Si) calculated by Gaussian 09 are adjusted during scaling procedure with MOLVIB and were converted to relative Raman intensity (I_i) using