

Molecular structure, vibrational spectroscopic (FT-IR, FT-Raman), first order hyperpolarizability, NBO analysis, HOMO and LUMO analysis, thermodynamic properties of 3,5-dimethylbenzophenone by *ab initio* HF and density functional method

K. Chaitanya*, C. Santhamma, K. V. Prasad, and V. Veeraiiah

Molecular Spectroscopy Laboratories, Department of Physics, Andhra University, Visakhapatnam, India

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Abstract. The FT-IR solid phase ($4000\text{--}450\text{ cm}^{-1}$) and FT-Raman spectra ($3500\text{--}100\text{ cm}^{-1}$) of 3,5-Dimethylbenzophenone (3,5-DMBP) was recorded at room temperature. Density functional theory calculations with B3LYP/6-31+G(*d*, *p*) basis sets was used to determine ground state molecular geometries (bond lengths and bond angles), harmonic vibrational frequencies, infrared intensities, Raman activities and bonding features of this compound. The assignments of the vibrational spectra have been carried out with the help of normal co-ordinate analysis (NCA) following the Scaled Quantum Mechanical Force Field methodology (SQMFF). The first order hyperpolarizability (β_0) of this novel molecular system and related properties (β , α_0 and $\Delta\alpha$) of DMBP are calculated using HF/6-31+G(*d*,*p*) method on the finite-field approach. Stability of the molecule have been analyzed using NBO analysis. The calculated first hyperpolarizability shows that the molecule is an attractive molecule for future applications in non-linear optics. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule. Mulliken population analysis on atomic charges is also calculated. On the basis of vibrational analyses, the thermodynamic properties of the title compounds at different temperatures have been calculated. Finally the calculations results were applied to simulate infrared and Raman spectra of the title compound which show good agreement with observed spectra.

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*Corresponding author. *Email address:* cskcmail@gmail.com (K. Chaitanya)

1 Introduction

Benzophenone and its derivatives were of great interest because of their extensive application in varied areas, such as medicine [1–3] and photochemistry [4, 5]. These molecules possess non-centro symmetry and hence they are widely used in the synthesis of molecules having non-linear responses [6, 7]. The investigation on the structure and fundamental vibrations of benzophenone and its derivatives are still being carried out increasingly. The inclusion of an electron donating methyl group in aromatic ring leads to the variation of charge distribution in the molecule, and consequently affects the structural, electronic and vibrational parameters.

The vibrational spectra of benzophenone and its derivatives were measured and discussed by several authors [8–23]. While the standard molar gas-phase enthalpies of formation, at $T = 298.15$ K, of 2-, 3-, and 4-methylbenzophenone [24] and 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-, 2,2'-, 2,3'-, 2,4'-, 3,3'-, 3,4'- and 4,4'- dimethylbenzophenone [25] have been studied both by experimental and computational techniques, there comprehensive normal-mode analysis is unavailable. Crystal, molecular structure and vibrational spectra of α -4-methylbenzophenone by density functional theory calculations have been carried out by Sasiadek *et al.* [26]. Literature survey reveals that so far there is no complete vibrational spectral study for the title compound 3,5-DMBP.

In the present study we have investigated the optimized geometries, atomic charges and vibrational spectra for the 3,5-DMBP molecule in optimum energy conformation and analyze the influences of methyl group to the geometry and different normal modes of the benzophenone molecule. The vibrational frequencies of the title compound are assigned to their corresponding normal mode vibration using band intensities and potential energy distributions (PEDs). The redistribution of electron density (ED) in various bonding, antibonding orbitals and $E(2)$ energies had been calculated by natural bond orbital (NBO) analysis to give clear evidence of stabilization originating from the hyper conjugation of various intra-molecular interactions. The study of HOMO, LUMO analysis have been used to elucidate information regarding charge transfer within the molecule. Finally, the thermodynamic properties of the optimized structures were obtained theoretically from the harmonic vibrations.

2 Experimental

Fourier transform infrared spectra of the title compound is measured at the room temperature in the region $4000\text{--}400\text{ cm}^{-1}$ using a BRUKER IFS -66 V FTIR spectrometer at a resolution of $\pm 1\text{ cm}^{-1}$ equipped with a MCT detector, a KBr beam splitter and globar source. The FT-Raman spectrum of 3,5-DMBP is recorded on a BRUKER IFS -66 V model interferometer equipped with FRA-106 FT-Raman accessory in the $3500\text{--}100\text{ cm}^{-1}$ Stokes region using the 1064 nm line of a Nd: YAG laser for excitation operating at 200 mW power. The reported wave numbers are believed to be accurate within $\pm 1\text{ cm}^{-1}$. The molecule 3, 5-dimethylbenzophenone was newly synthesized by Wang *et al.* [27].