Journal of Molecular Structure 1111 (2016) 151–156

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Molecular structure, vibrational spectral assignments (FT-IR and FT-RAMAN), NMR, NBO, HOMO-LUMO and NLO properties of O-methoxybenzaldehyde based on DFT calculations

P. Vennila [a], [*], M. Govindaraju [b], G. Venkatesh [c], C. Kamal [c]

[a] R&D Centre, Bharathiar University, Coimbatore 641 046, India
[b] Arignar Anna Government Arts College, Namakkal 638 052, India
[c] Department of Chemistry, VSA Group of Institutions, Salem 636 010, Tamilnadu, India

ARTICLE INFO

Article history:
Received 17 November 2015
Received in revised form
26 January 2016
Accepted 26 January 2016
Available online 1 February 2016

Keywords:
Density functional theory
FT-Raman
FT-IR
First-order hyperpolarizability
Electronic excitation energy

ABSTRACT

Fourier transform – Infra red (FT-IR) and Fourier transform – Raman (FT-Raman) spectroscopic techniques have been carried out to analyze O-methoxy benzaldehyde (OMB) molecule. The fundamental vibrational frequencies and intensity of vibrational bands were evaluated using density functional theory (DFT). The vibrational analysis of stable isomer of OMB has been carried out by FT-IR and FT-Raman in combination with theoretical method simultaneously. The first-order hyperpolarizability and the anisotropy polarizability invariant were computed by DFT method. The atomic charges, hardness, softness, ionization potential, electronegativity, HOMO-LUMO energies, and electrophilicity index have been calculated. The ^{13}C and ^{1}H Nuclear magnetic resonance (NMR) have also been obtained by GIAO method. Molecular electronic potential (MEP) has been calculated by the DFT calculation method. Electronic excitation energies, oscillator strength and excited states characteristics were computed by the closed-shell singlet calculation method.

1. Introduction

Benzaldehyde derivatives are the most important molecules, having chemical and biological properties. These derivatives find extensive applications in cosmetic, textiles and biomaterial industries. In addition, they have anti-microbial and anti-cancer activities. Methoxybenzaldehyde (MBZ), a benzaldehyde derivative, is widely used in medicinal, fragrance and flavor industries. MBZ are great interest in the synthesis of pharmaceuticals and perfumery compounds. Anjaneyulu et al. have been reported the vibrational spectra and normal co-ordinate analysis of substituted benzaldehyde derivatives using valence force field theory [1]. Sing and his co-workers reported FT-IR and FT-Raman spectra of hydroxyl substituted benzaldehyde [2]. Kalaiselvan et al. have examined 2-nitro and 4-nitro benzaldehydes using *ab-initio* calculations [3]. Also several other researchers have analyzed benzaldehyde derivatives using DFT with B3LYP/6-31 + G* basis set [4,5]. Hiremath et al. have been investigated vibrational spectra and normal coordinate analysis of 3-chloro-4-methoxy benzaldehyde [6]. Further, they have calculated the electronic energy of O-cis and O-trans isomer of 2-bromo-5-fluoro benzaldehyde [7]. Ribeiro-Claro et al. have discussed the formation of inter/intra-molecular hydrogen bonding (CH···O) and dimer formation in 2 methoxy and 4 methoxy benzaldehydes [8]. From the literature, it is clear that the derivatives of benzaldehyde have significant spectral properties. In a continuation to study the spectral response of benzaldehyde derivatives, the spectral and theoretical analyses of OMB have been carried out in the present study. Hence, the study on OMB will bring out a new facet of application of the benzaldehyde derivatives and will include one more new compound having significant biological activities in future. Thus, the present work deals with complete vibrational assignments of FT-IR and FT-Raman intensities, optimized geometry, DFT combined with quantum chemical calculations, the molecular properties and first-order hyperpolarizability of OMB. MEP is an effective tool in assessing the reactivity of molecules towards positively or negatively charged reactants.

---

[*] Corresponding author.
E-mail address: vennilaindhu84@gmail.com (P. Vennila).

http://dx.doi.org/10.1016/j.molstruc.2016.01.068
0022-2860/© 2016 Elsevier B.V. All rights reserved.

2. Experimental methods and computational details

OMB has been purchased in analytical grade from Lancaster Chemical Company, UK. FT-IR spectra for the compound have been measured in the region 4000–400 cm^{-1}, at a resolution of ±1 cm^{-1} with 16 scan number using BRUKER IFS 66V vacuum FT spectrometer, equipped with an MCT detector, a KBr beam splitter and global source. The FT-Raman spectra were recorded on the same instrument with FRA 106 Raman accessories in the region 4000–100 cm^{-1}. The source used to record FT-Raman spectra was Nd:YAG laser operating at 200 mW power with 1064 nm excitation.

The quantum chemical calculations have been carried out by DFT method using the GAUSSIAN 09W program [9] by B$_3$LYP functional supplemented with the standard $6-311+G^{**}$ basis set [10]. The Cartesian representation of the theoretical force constants has been computed at the completely optimized geometry by assuming C_s point group symmetry. Scaling of the force field has been carried out according to the SQM procedure [11] using selective scaling in the normal internal coordinate analysis. Force field transformation and the subsequent normal coordinate analysis with the least squares refinement of the scaling factors, calculation of Total Energy Distribution (TED) and prediction of IR and Raman Intensities were carried out using PC with the MOLVIB program written by Sundius [12]. The Total energy distribution (TED) elements provide a measure of each internal coordinate's contributions to the normal coordinate. To obtain the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a bandwidth of 10 cm^{-1}. The Raman intensities have been interpreted by following the equation shown below [13,14].

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i[1 - exp(-hcv/KT)]} \qquad (1)$$

Here, υ_0 represents exciting frequency (in cm^{-1}), υ_i represents the vibrational wave number of the normal mode; h, c and k are universal constants, f is normalization factor.

The MEP is typically visualized through mapping its values onto the surface reflecting the molecules boundaries. In order to calculate the MEP of OMB, the geometry of the molecule was optimized at the B3LYP/$6-31+G^{*}$ basis set. Visualization of the MEP then requires three more steps: (1) calculation of the outer envelope of OMB as defined through a constant value of electron density, (2) calculation of the MEP at a number of points around the molecule and (3) mapping of the MEP on the molecular surface using a colour coded scheme.

3. Results and discussion

3.1. Molecular geometry and conformers

In order to confirm the stable isomer, the molecular structure was optimized using DFT theory. The electronic calculations have been carried out for different possible OMB conformers of O-cis and O-trans isomer are shown in Fig 1. The global minimum energy is given in Table S1 in supplementary material. From the table, it is clear that the trans-OMB is more stable than the cis-OMB, since trans isomer has lower energy than cis isomer. The molecular structure of the O-trans isomer of OMB has C_s point group of symmetry. The maximum numbers of possible active visible fundamental vibration of non linear molecules which contain oxygen atom are equal to (3N-6) degree of freedom [15]. But in the present study, no such degrees of freedom have been observed. This is due to the C_s point group symmetry of OMB. Table 1 shows the optimization bond length, bond angle and dihedral angle for stable isomer of OMB. Ribeiro Claro et al. reported previously that, there has been a formation of dimer of 2MEOB due to the existence of supra molecular interaction in solid and liquid phase [8]. The results of present study are agreed with the previous report. The effect of aldehyde rotation of $\gamma C = O$ group higher wave number 1786 cm^{-1} assign to carbonyl group, lower wave number 1782 cm^{-1} assign to hydrogen bonding having carbonyl atom.

3.2. Vibrational analysis

The FT-IR and FT-Raman spectroscopic analyzes have been recorded to investigate the vibrational responses of functional groups of OMB. The vibrational assignments viz., IR, Raman intensities and normal mode descriptions of OMB are listed in supplementary material (Table S3). An illustration of the obtained and fitted FT-IR and FT-Raman spectra of OMB are shown in Fig 2 & Fig 3. The OMB molecule has 48 normal modes of vibrations, 33 in–plane of vibrations and residual 15 out-of-plane of vibrations. The 48 normal modes of vibrations were distributed as $\Gamma_{3N\text{-}6} = 33$ A' (in-plane) + 15 A″ (out-of-plane) and is in agreement with C_s symmetry. The 48 normal modes of vibrations were active in IR absorption and Raman. The normal coordinate analysis (NCA) has been discussed to describe the vibrational modes of OMB.

The values calculated for 61 standard internal coordinates containing 13 redundancies are listed in Table S2 in supplementary material. Fogarasi et al. have reported the linear combinations of internal coordinates were constructed to a non-redundant set of local symmetry coordinates shown in Table 2 [16]. The vibrational coordinates used in all calculations were transformed by DFT force fields. The values of root mean square (RMS) for the obtained frequencies have been computed from the following equation,

$$RMS = \sqrt{\frac{1}{n-1}\sum_{i}^{n}\left(U_i^{calc} - U_i^{\exp}\right)^2} \qquad (2)$$

The error found in RMS frequencies was found to be 104 cm^{-1} for OMB. The RMS deviation of least square refinement algorithm was as 6.8 cm^{-1}.

3.2.1. C–H vibrations

The band appeared at 3300–3100 cm^{-1} indicated the presence of aromatic C–H stretching vibrations. The absorption bands at 3237, 3235, 3232, 3212, 3210, 3208 cm^{-1} and FT-Raman bands at 3225, 3222, 3221 cm^{-1} were assigned to C–H stretching [16]. Overtone and combination bands due to the C–H out-of-plane is appeared in the region 1670–1450 cm^{-1}. This absorption patterns observed at 1514, 1512 and 1509 cm^{-1} for FT-IR and 1497, 1495and 1492 cm^{-1} for FT-Raman.

3.2.2. C–C vibrations

The ring C–C stretching vibrations are usually occur in the region 1350-1240 and 1700-1585 cm^{-1}. The C–C stretching vibrations of OMB are observed at 1661, 1658, 1657, 1543, 1541, 1514, 1512 and 1509 cm^{-1} in the FT-IR spectrum and 1641, 1639 and 1637 cm^{-1} in FT-Raman spectrum. The C–C stretching bands are observed at 1358, 1357, 1355, 1295, 1294 and 1290 cm^{-1} in FT-IR spectrum and 1331, 1329, 1325, 1229, 1228 and 1224 cm^{-1} in FT-Raman spectrum [17].

3.2.3. Ring vibrations

In the present study the bands ascribed at 1083, 1082, 1079, 810, 809, 804 cm^{-1} are assigned to ring in-plane and 996, 994, 991, 971, 969, 965, 801, 778 and 776 cm^{-1} have been designated to ring out-plane bending modes, respectively.