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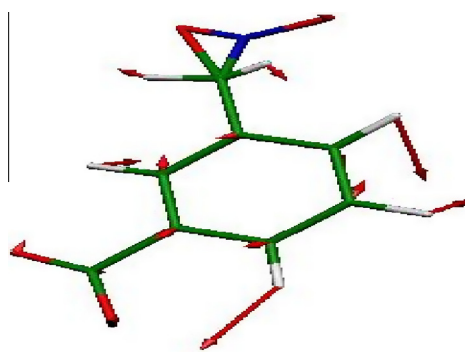
The spectroscopic (FTIR, FT-Raman and UV–Vis spectra), DFT and normal coordinate computations of m-nitromethylbenzoate

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HIGHLIGHTS

- The FT-IR, FT-Raman and UV–Vis spectra were recorded and analyzed for the compound.
- Quantum chemical calculations HF/DFT using 6-31G(d,p) and 6-31+G(d,p) basis sets were carried out.
- The complete vibrational assignment and spectroscopic analysis have been carried out.
- The first order hyperpolarizability and HOMO, LUMO energy gap were theoretically predicted.
- The NBO analysis explained the intramolecular hydrogen bonding.

GRAPHICAL ABSTRACT



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ABSTRACT

A combined experimental and theoretical study on molecular structure, vibrational spectra, NBO and UV-spectral analysis of m-nitromethylbenzoate (MNMB) has been reported in the present work. The FT-IR solid phase ($4000\text{--}400\text{ cm}^{-1}$) and FT-Raman spectra ($3500\text{--}100\text{ cm}^{-1}$) of MNMB was recorded. The molecular geometry, harmonic vibrational frequencies and bonding features of MNMB in the ground-state have been calculated by using the density functional method B3LYP with 6-31G(d,p) and 6-31+G(d,p) basis sets. 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). Stability of the molecule arising from hyperconjugative interactions, charge delocalization has been analyzed using natural bond orbital (NBO) analysis. The results show that charge in electron density (ED) in the σ^* antibonding orbitals and $E(2)$ energies confirms the occurrence of ICT (Intra-molecular Charge Transfer) within the molecule. The UV spectrum was measured in ethyl acetate solution. The energy and oscillator strength calculated by Time-Dependent Density Functional Theory (TD-DFT) result complements the experimental findings. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule. Finally the calculation results were applied to simulated infrared and Raman spectra of the title compound which show good agreement with observed spectra.

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Introduction

Benzene rings are components of many important natural products and other useful organic compounds. Therefore, the ability to put substituents on a benzene ring, at specific positions relative to each other, is a very important factor in synthesizing many organic compounds. The two main reaction types used for this are both substitutions: Electrophilic Aromatic Substitution (EAS) and Nucleophilic Aromatic Substitution (NAS). The benzene ring itself is electron-rich, which makes NAS difficult, unless there are a number of strongly electron-withdrawing substituents on the ring. EAS, on the other hand, is a very useful method for putting many different substituents on a benzene ring, even if there are other substituents already present. M-nitromethylbenzoate is synthesized using EAS method whose boiling point is 279 °C and melting point 79–80 °C and used many pharmaceutical and biological applications. [1,2].

It is well known that quantum chemical methods are useful for adequate prediction and interpretation of vibrational spectra [3]. With the recent progress in developing useful approximate functional and availability of versatile software, density functional theory (DFT) has become a popular and successful approach for the computation of molecular structure, vibrational wavenumbers, and energies of chemical reactions [4]. The complete vibrational analysis of MNMB was performed by combining the experimental and theoretical information using Pulay's density functional theory (DFT) based on scaled quantum chemical approach [5]. The DFT calculations are also reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity effects [6–8]. The DFT methods are increasingly used by spectroscopists for modeling molecular properties that includes equilibrium structure, vibrational frequencies, and intensities [9].

Literature survey reveals that so far there is no complete theoretical and experimental study for the title compound MNMB. In this work, we mainly focused on the detailed spectral assignments and vibrational thermodynamic properties basing on the experimental Fourier transform infrared (FT-IR) and Fourier transform Raman (FT-Raman) spectra as well as DFT/B3LYP calculations for MNMB. The redistribution of electron density (ED) in various bonding, antibonding orbitals and $E(2)$ energies have been calculated by natural bond orbital (NBO) analysis to give clear evidence of stabilization originating from the hyper conjugation of various intramolecular interactions. The study of HOMO, LUMO analysis has been used to elucidate information regarding charge transfer within the molecule. Finally, the UV-Vis spectra and electronic absorption properties were explained and illustrated from the frontier molecular orbitals. Here, the calculated results have been reported in the text. The experimental and theoretical results supported each other, and the calculations are valuable for providing insight into the vibrational spectra and molecular properties.

Experimental details

The fine polycrystalline sample of MNMB was obtained from the Lancaster chemical company, UK and used as such for the spectral measurements. The room temperature Fourier transform infrared spectrum of the title compound was measured in the 4000–400 cm^{-1} region at a resolution of $\pm 1 \text{ cm}^{-1}$ using a BRUKER IFS-66v FTIR spectrometer equipped with dual detection: a cooled MCT detector for the mid-IR. KBr pressed pellet technique was used in the spectral measurements. The FT-Raman spectra of MNMB was recorded on a BRUKER IFS-66v model interferometer equipped with an FRA-106 FT-Raman accessory in the 3500–100 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 UV absorption spectra of MNMB were examined in the range 200–700 nm using the Shimadzu 1800, UV-Vis recording spectrometer. The UV pattern is taken from a 10^{-5} M solution of MNMB, dissolved in ethyl acetate.

Computational details

The entire calculations were performed at Hartree-Fock (HF) and density functional (DFT) levels using Gaussian 03 W [10] program package, invoking gradient geometry optimization [11]. Initial geometry generated from the standard geometrical parameters was minimized without any constraint on the potential energy surface at HF level adopting the standard 6-31G(d,p) and 6-31+G(d,p) basis set. This geometry was then re-optimized again at DFT level employing the Becke 3LYP keyword, which invokes Becke's three-parameter hybrid method [12] using the correlation function of Lee et al. [13]; implemented with the same basis set. The optimized structural parameters were used for the vibrational frequency calculations at DFT level to characterize all the stationary points as minima. The calculated frequencies are scaled according to the work of Rauhut and Pulay [14,15], a scaling factor of 0.963 for B3LYP and similarly for HF were scaled by a value of 0.891 [16].

According to SQM procedure using selective scaling in the natural internal coordinate representation [5,17]. The transformation of force field; subsequent normal coordinate analysis and calculation of the TED were done on a PC with the MOLVIB program (version V7.0-G77) written by Sundius [18–20]. By the use of GAUSSVIEW molecular visualization program [21] along with available related molecules; the vibrational frequency assignments were made by their TED with a high degree of confidence. The TED elements provide a measure of each internal coordinate's contributions to the normal coordinate.

Prediction of Raman intensities

The Raman activities (S_i) calculated with the GAUSSIAN 03 W program were subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [22,23],

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i [1 - \exp(-hc v_i / k_b T)]}$$

where v_0 is the exciting frequency in cm^{-1} , v_i the vibrational wave number of the i th normal mode, h , c and k_b are the fundamental constants and f is a suitably chosen common normalization factor for all the peak intensities.

Results and discussion

Molecular geometry

The labeling of atoms in MNMB is given in Fig. 1. The structural parameters obtained by ab initio HF and DFT/B3LYP levels with the 6-31G(d,p) and 6-31+G(d,p) basis sets are reported in Table 1. All the geometries determined belong to a true minimum proven by real wavenumbers in the vibrational analysis. Compared with HF and B3LYP levels of the bond lengths and bond angles differences between theoretical approaches have been shown in Figs. 2 and 3, respectively. The optimized geometry reveals that NO_2 group substituted in meta position of benzene ring is laying slightly out-of-plane. The benzene ring appears to be little distorted with ($\text{C}_4\text{--C}_3$) and ($\text{C}_4\text{--C}_5$) bond lengths exactly at the substitution place $\sim 1.39 \text{ \AA}$ and $\sim 1.40 \text{ \AA}$ by B3LYP, HF method smaller than the remaining bonds ($\text{C}_3\text{--C}_2$), ($\text{C}_6\text{--C}_5$), ($\text{C}_7\text{--C}_6$) and ($\text{C}_7\text{--C}_2$).

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