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Spectroscopic and quantum chemical analysis of Isonicotinic acid methyl ester

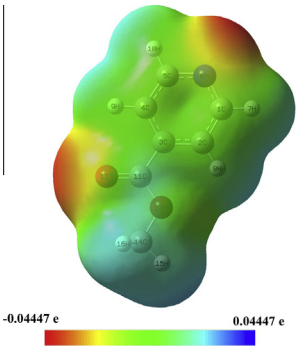
D. Shoba [a,b], S. Periandy [c], M. Govindarajan [d,*], P. Gayathri [a]

[a] Department of Physics, Periyar Maniammai University, Thanjavur, India
[b] Department of Physics, Alpha College of Engineering & Technology, Puducherry, India
[c] Department of Physics, Tagore Arts College, Puducherry, India
[d] Department of Physics, Bharathidasan Government College for Women, Puducherry, India

HIGHLIGHTS

- Vibrational properties of Isonicotinic acid methyl ester was examined by FT-IR, FT-Raman and NMR techniques and DFT methods.
- The geometrical parameters are in agreement with experimental values.
- NLO and NBO analysis of the molecule were studied.
- HOMO and LUMO energies, molecular electrostatic potential distribution of the molecule were calculated.

GRAPHICAL ABSTRACT



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ABSTRACT

In this present study, an organic compound Isonicotinic acid methyl ester (INAME) was structurally characterized by FTIR, FT-Raman, and NMR and UV spectroscopy. The optimized geometrical parameters and energies of all different and possible conformers of INAME are obtained from Density Functional Theory (DFT) by B3LYP/6-311++G(d,p) method. There are three conformers (SI, SII-1, and SII-2) for this molecule (ground state). The most stable conformer of INAME is SI conformer. The molecular geometry and vibrational frequencies of INAME in the ground state have been calculated by using HF and density functional method (B3LYP) 6-311++G (d,p) basis set. Detailed vibrational spectral analysis has been carried out and assignments of the observed fundamental bands have been proposed on the basis of peak positions and relative intensities. The computed vibrational frequencies were compared with the experimental frequencies, which yield good agreement between observed and calculated frequencies. A study on the electronic properties, such as HOMO and LUMO energies were performed by time independent DFT approach. Besides, molecular electrostatic potential (MEP) and thermodynamic properties were performed. The electric dipole moment (μ) and first hyper polarizability (β) values of the investigated molecule were computed using ab initio quantum mechanical calculations. The calculated results show that the INAME molecule may have microscopic nonlinear optical (NLO) behavior with non zero values. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) chemical shifts of the molecule were calculated by gauge independent atomic orbital (GIAO) method.

* Corresponding author. Tel.: +91 9443525988.
E-mail address: govindarajan64@gmail.com (M. Govindarajan).

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Introduction

Isonicotinic acid methyl ester (INAME) is a natural heterocyclic aromatic organic compound. It is a methyl acetate substituted derivative of pyridine. It is also called as methyl; 4-pyridylacetate with molecular formula $C_8H_9NO_2$ has been isolated from the basic fraction of coal tar and from bone oil. Methyl pyridines have been used for synthesis of polymers with thermal and fire resistance properties. It has been detected in waste water from oil shale processing sites and former creosoting facilities. It has been evaluated for use as a food additive owing to its nutty aroma when present in solution at very low concentrations; however the neat solvent has a pungent, noxious odor [1–5]. INAME is weakly nucleophilic, due to the steric effects of the two methyl groups on the ring nitrogen. Pyridine acid and its derivatives have biological activities. Many drugs found with pyridine compounds. Bromopyridine find wide application in pharmacological industry and in chemical laboratories. Therefore, the spectral and vibrational analysis of substituted pyridine has been the subject of several investigations. Chattopadhyay et al. have been studied the surface-enhanced Raman spectroscopy of 2,5-dibromopyridine and 2,6-dibromopyridine. Halogen substituted pyridine compounds were studied by Green et al. [6–12].

The molecule under study is an isomer of nicotinic. Isonicotinoyl hydrazide (Isoniazid) is one of the anti-tuberculosis drugs and used to kill the mycobacterium tuberculosis. Isonicotinoyl hydrazone derivatives containing heterocyclic moiety have found. It is also used in manufacturing pharmaceuticals and agrochemicals. Niacin acts to reduce plasma cholesterol as a vasodilator and to treat pellagra and also is used for the Prophylaxis. Many substituted pyridines are involved in bioactivities with applications in pharmaceutical drugs and agricultural products (pyridine derivatives act as anesthetic agents, drugs for certain brain diseases, and drugs for treating neuronal damage caused by stroke. Nicotinic acid and its derivatives have biological activities; have been studies extensively over the past decade. The structure of many of the complexes that have been reported show nicotinic acid and its derivatives acting as bridging ligands through the carboxylate group and pyridyl N atom [13]. Nicotinic acid and its complexes with different metals were thoroughly investigated in different methods [14,15].

Extensive experimental and theoretical investigations have focused on elucidating the structure and normal vibrations of nicotinic acid derivatives. Vibrational assignment based FT-IR and Raman spectra and theoretical DFT calculations have been studied for nicotinic and isonicotininc acids [16]. Karaback and Kurt [17] investigated vibrational modes of 6-chloro nicotinic acid by both experimental and theoretical methods. Nagabalasubramanian et al. [18] investigated conformational stability and vibrational modes of nicotinic acid ethyl ester using both experimental and theoretical methods. Sala et al. [19] investigated vibrational modes of nicotinic acid by both experimental and theoretical methods; however, literature survey reveals that to the best of our knowledge, neither quantum chemical calculations nor the vibrational spectra of Isonicotinic acid methyl ester have been reported, as yet. Therefore the present investigation was under taken to study the vibrational spectra of this molecule completely and to identify the various modes with greater wave number accuracy. The interaction energies, NMR spectral analysis, molecular electrostatic potential, thermodynamic and nonlinear optical properties of the title compound were investigated at the B3LYP/6-311++G (d,p) level. In general, the DFT methods yield sufficiently good and consistent results at moderate computational costs. Due to some systematic errors, such as the neglect of anharmonicity and electron correlations, the calculated frequencies are scaled to compensate to the approximate treatment of electron correlation for basis set deficiencies and for anharmonicity effects.

Experimental details

The spectra of Isonicotinic acid methyl ester was purchased from spectral library of Sigma–Aldrich Chemicals, USA. The FT-IR spectrum of the compound was recorded in Perkin-Elmer 180 Spectrometer in the range of 4000–400 cm^{-1}. The spectral resolution is ±2 cm^{-1}. The FT-Raman spectrum of the compound was also recorded in the same instrument with FRA 106 Raman module equipped with Nd: YAG laser source operating at 1.064 μm line widths with 200 mW powers. The spectra were recorded with scanning speed of 30 cm^{-1} min^{-1} of spectral width 2 cm^{-1}. The frequencies of all sharp bands are accurate to ±1 cm^{-1}.

Quantum chemical calculations

The entire quantum chemical calculations have been performed at HF and DFT (B3LYP) methods using the Gaussian 03W program [20]. The optimized geometrical parameters have been evaluated for the calculations of vibrational frequencies at different levels. The computed vibrational modes do not contain any imaginary frequency. Thus, the structures obtained are real minima on the potential energy surface. As a result, the vibrational calculated frequencies, reduced masses, force constants, infrared intensities, Raman activities and depolarization ratios are obtained. In order to improve the calculated values in agreement with the experimental values, it is necessary to scale down the calculated harmonic frequencies. Hence, the vibrational frequencies are scaled using 0.906 for HF and 0.953 used for B3LYP methods [21,22]. After scaling the calculated frequencies, the deviation from the observed values are less than 10 cm^{-1} with a few exceptions. Gauss view program [23] has been considered to get visual animation and for the verification of the normal modes assignment.

Results and discussion

Potential energy surface (PES) scan, conformational isomers

The INAME has one substituent group (carboxyl group) attached to the pyridine ring and methoxy group. The carboxyl group was chosen to investigate the possible conformers of the molecule under investigation. In order to describe conformational flexibility of the title molecule, the energy profile as a function of C—C—C—O torsion angle was achieved with AM1 method (Fig. 1). All the geometrical parameters were simultaneously relaxed during the calculations while the C—C—C—O torsional angle was varied in steps of 10°. As can be seen from Fig. 1, the local minima at 0° (or 360°) and 180° were obtained for S1 (C_1) and S2 (C_1 and Cs) conformers, respectively, for T(C—C—C—O). This result shows that INAME molecule has three possible structures; depend on the positions of the carbon atom bonded to oxygen and symmetry, whether it is directed away from or toward the ring. The resulted potential energy curve depicted in Fig. 1 shows S1 (C_1) form for minimum energy. In this study, calculations were done for two conformers (S1 and S2) of title molecule, however, tables and figures were prepared only for the most stable conformer S1(C_1 form).

Geometrical analysis

The molecular geometry states the position of the atoms in terms of bond lengths, bond angles and dihedral angles with