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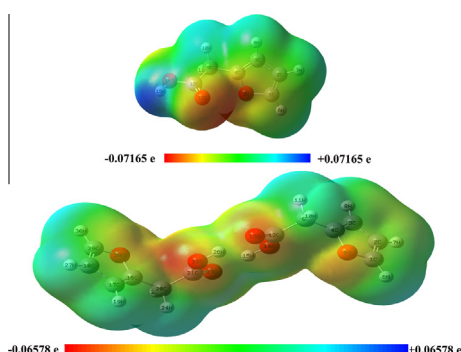
Molecular structure and vibrational spectroscopic studies on 2-furanacetic acid monomer and dimer

H. Ghalla^a, M. Govindarajan^{b,*}, H.T. Flakus^c, N. Issaoui^a, S.J. Yaghmour^d, B. Oujia^{a,d}^a University of Monastir, Quantum Physics Laboratory, Faculty of Science, Monastir 5079, Tunisia^b Department of Physics, BGCW College, Puducherry, India^c Institute of Chemistry, University of Silesia, 9 Szkolna Street, 40-006 Katowice, Poland^d King Abdulaziz University, Faculty of Science, Saudi Arabia

HIGHLIGHTS

- Molecular structure of 2-furanacetic acid and its dimer were investigated.
- Spectroscopic properties of molecule were examined by FT-IR and FT-Raman techniques.
- The complete vibrational assignments are performed on the basis of normal coordinate analysis.
- NLO properties and NBO analysis were investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, molecular geometries and fundamental vibrational frequencies of 2-furanacetic acid (2FAA) and its hydrogen bonded dimer were investigated using DFT/B3LYP method with 6-311++G(d,p) as basis set. The FT-infrared and FT-Raman spectra of the 2FAA compound were recorded in the region 4000–400 cm^{-1} . The theoretical wavenumbers were scaled and compared with experimental FT-IR and FT-Raman spectra. Complete vibrational assignments and analysis of the fundamental modes of monomer and dimer structures were performed on the basis of the potential energy distribution (PED) calculations. A study on the electronic properties, such as excitation energies, oscillator strength, wavelengths, HOMO and LUMO energies, are performed by time-dependent DFT (TD-DFT) approach. Molecular stability arising from hyperconjugative interactions and charge delocalization has been analyzed using Natural Bond Orbital (NBO) analysis. Topological parameters such as electron density and its Laplacian at bond critical points (BCP) of O–H and O...H contact bonds were analyzed in details with the help of the atoms in molecules (AIM) approach in order to study the intermolecular hydrogen bonding. The nonlinear optical properties of the title molecule have been investigated. Moreover, molecular electrostatic potential (MEP) surface was plotted for predicting sites and relative reactivities towards electrophilic and nucleophilic attack. The nonlinear optical properties were reported and compared with that of the urea. The thermodynamic properties like heat capacity, entropy, and enthalpy have been calculated for the molecule at different temperatures.

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* Corresponding author. Tel.: +91 9443525988.

E-mail address: govindarajan64@gmail.com (M. Govindarajan).

Introduction

Organic compounds containing five-membered aromatic heterocyclic rings are widely distributed in nature and often play an important role in various biochemical processes. Furan and its derivatives have been extensively studied because of the presence of these units in a variety of natural and synthetic products. Many of the furan natural products are known for their inspiring pharmacological activities, such as cytotoxic and antitumor properties [1,2], antispasmodic [3] and anti-feeding activities [4]. In addition, furan carboxylic acids find applications in the agro-chemical field as compounds which enhance plant resistance to stress [5] and in polymer chemistry [6] for nylon preparation. Further, it possesses high optical nonlinearity which can be used in the fabrication of optical and electroluminescent devices [7]. The synthesis of the title compound is relatively sensitive to strong mineral acids, particularly the halogen acids. So, the 2FAA can be synthesized from furfural without using any reaction which involves such acids. The 2-FAA product, as a white crystalline solid, was obtained following a series of reactions given by Mabel et al. [8]. The 2FAA crystallizes in space-symmetry group $P2_1/c$, with four molecules per unit cell ($Z=4$) with $a=13.0525(4)$ Å; $b=4.85360(10)$ Å; $c=9.4107(3)$ Å, $\beta=103.832(3)^\circ$ [9]. In 2FAA crystals, the carboxylic group of one molecule form centrosymmetric cyclic dimers with carboxylic group of the adjacent molecule through the intermolecular O—H...O hydrogen bonds. The hydrogen bondings form an infinite sheet. Hydrogen bonds play an important role in the stabilization of the molecular structure.

Flakus et al. have reported experimental and theoretical study of polarized IR spectra of 2FAA crystal measured at 293 and 77 K in the ν_{O-H} and ν_{O-D} band frequency ranges [9]. They studied the role of the electronic structures of carboxylic acid molecules in the generation of IR spectra of cyclic hydrogen bond dimers. The temperature effects and the generation mechanism of the intensity distribution patterns in the ν_{O-H} and ν_{O-D} bands in the spectra of diverse carboxylic acid crystals are also investigated. In their theoretical approach, Flakus et al. have assumed that the main ν_{O-H} and ν_{O-D} band shaping mechanism involved strongly anharmonically coupled to the high-frequency proton (or deuteron) stretching vibrations and the low-frequency O...O hydrogen bridge stretching vibrational motions. Their calculation of the hydrogen bond system IR spectra in terms of the “strong-coupling” model allows to obtain results fairly comparable with the results of the spectra calculation performed using the “relaxation” theory [10,11].

In recent years, among the computational methods calculating the electronic structure of molecular systems, DFT method has been favorite one due to its great accuracy in reproducing the experimental values of molecular geometry, vibrational frequencies, atomic charges, dipole moment, thermodynamic properties etc. [12–25]. Literature survey reveals that to the best of our knowledge, neither DFT investigations, nor vibrational spectroscopic and electronic structures of 2FAA have been reported yet. Theoretical study on the structure and vibrational spectra of 2FAA molecule will help in understanding the property of the title molecule in depth insight. So, in the present work the geometrical parameters, vibrational wavenumbers, NBO analysis [26], electrostatic potential surface were calculated by using DFT-B3LYP method with 6-311++G(d,p) as basis set. The HOMO and LUMO analysis have been used to elucidate information regarding charge transfer within the molecule. Conscientious attention has been focused on the effects of intermolecular O—H...O hydrogen bonding, on the distances, calculated frequencies and nature of hydrogen bonding by calculating topological parameters at the bond critical points using AIM theory [27,28]. Moreover, the thermodynamic and nonlinear optical properties of the title molecule were investigated.

FT-infrared and FT-Raman measurements

The compound under investigation (2FAA) was obtained from Aldrich chemicals and used as such to record FT-IR and FT-Raman spectra. The FT-IR and FT-Raman spectra of 2FAA were recorded at room temperature in the region 4000–400 cm^{-1} using CaF₂ windows. The sample was prepared using a KBr pellet technique. The crystal was selected to the experiment by use of a thin, tin plate diaphragm with a 1.5 mm diameter hole, and then IR spectra of these crystalline fragments were measured by a transmission method. The IR spectrum was measured with the Nicolet Magna 560 FT-IR spectrometer. The Raman spectrum of 2FAA were measured with the use of the Bio-Rad FTS-175C FTIR spectrometer at the 1 cm^{-1} resolution.

Quantum chemical calculations

The entire calculation for the monomer and hydrogen bonded dimer of 2FAA were performed by DFT/B3LYP method with 6-311++G(d,p) as basis set. All the calculation was performed using Gaussian 03W program package [29] with the default convergence criteria without any constraint on the geometry. At the optimized geometries of the 2FAA monomer and dimer structures no imaginary frequency modes were obtained, therefore there is a true minimum on the potential energy surface was found. The interaction energies may be affected by the basis set superposition error (BSSE), which is usually corrected by the counterpoise (CP) correction method of Boys and Bernardi [30]. The vibrational assignments of the normal modes were performed on the basis of the PED calculations using the VEDA 4 program [31]. GaussView program [32] has been considered to get visual animation and also for the verification of the normal modes assignment. Since the DFT calculated frequencies are known to be higher than the experimental frequencies, due to the fact of electron correlation approximate treatment, anharmonicity effects and basis set deficiencies etc., they were scaled down using SPESCA program [33] and a comparison was made with the experimental values. The Raman activities (S_i) calculated by Gaussian 03W program package [29] were suitably converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [34,35]:

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i [1 - \exp(-hc\nu_i/kT)]} \quad (1)$$

Here ν_0 is the laser exciting wavenumber in cm^{-1} (in this work, we have used the excitation wavenumber $\nu_0 = 9398.5 \text{ cm}^{-1}$, which corresponds to the wavelength of 1064 nm of a Nd:YAG laser), ν_i is the vibrational wavenumber of the i th normal mode (cm^{-1}), while S_i is the Raman scattering activity of the normal mode ν_i . f (is a constant equal to 10^{-12}) is a suitably chosen common normalization factor for all peak intensities. h , k , c and T are Planck and Boltzmann constants, speed of light and temperature in Kelvin, respectively. The simulated spectra were plotted using a Lorentzian band shape with a half-width at half-height (HWHH) of 15 cm^{-1} . The NBO analysis was performed at the same level in order to understand various second order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of intermolecular delocalization of hyper conjugation. A topological analysis was performed with Bader's AIM theory using the AIM2000 package [36] for describing the O—H...O hydrogen bond interactions. The electronic properties, such as HOMO–LUMO energies, absorption wavelengths and oscillator strengths were calculated with TD-DFT method at B3LYP/6-311++G(d,p) level. The

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