Natural bond orbital analysis and vibrational spectroscopic studies of 2-furoic acid using density functional theory

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The molecular structure and vibrational spectra of 2-furoic acid have been calculated with the help of B3LYP density functional theory (DFT) using 6-31++G* as basis set. The solid phase FTIR and FT-Raman spectra of 2-furoic acid have been recorded in the range 4000-400 and 3500-50 cm⁻¹, respectively. On the basis of B3LYP calculations, the normal coordinate analysis have been performed to assign the vibrational fundamental frequencies according to potential energy distribution. The over estimation of the calculated wave numbers has been corrected by the aid of scaled quantum mechanical force field methodology. The computational frequencies are found to be in good agreement with the observed results. The stability of the molecule was analyzed using NBO analysis.

Keywords: Natural bond orbital, Vibrational spectroscopy, Density functional theory

1 Introduction

Furan is one of the simplest of aromatic molecules with a five membered heterocyclic oxygen-containing ring. Furan shows aromatic properties or aromaticity because the resulting \( \pi \) molecular orbital satisfies Huckel’s rule \((n=1 \text{ in } 4n + 2)\). 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\(^4\).

The compound 2-furoic acid was taken for the study since this lightest aromatic compound deserves special interest due to its extraordinary pharmaceutical and industrial importance\(^5\)-\(^8\). They exhibit anti-inflammatory, anti-irritant and anti-microbial effects, which make them more potent for topical applications in cosmetic and pharmaceutical formulations\(^5\). In addition, furan carboxylic acids find applications in the agro-chemical field as compounds which enhance plant resistance to stress\(^6\) and in polymer chemistry\(^7\) for nylon preparation. Further, it possesses high optical non-linearity which can be used in the fabrication of optical and electroluminescent devices\(^8\).

The structure determination of 2-furoic acid has been already reported by several researchers\(^9\)-\(^11\). The thermochemistry of 2-furoic acid has been studied by Roux et al\(^12\). The vibrational modes of 2-furoic acid have been assigned in the tetrahertz region by tetrahertz spectroscopy\(^13\). The infrared spectra of 2-furoic acid have also experimentally determined and studied\(^14\),\(^15\). Recently Uma et al. confirmed the presence of functional groups in 2 furoic acid by FTIR analysis and proved that the compound exhibits exceptional third order non-linear optical properties. Though, 2-furoic acid has been extensively studied by vibrational spectroscopic methods, density function calculations and normal coordinate analysis on this compound have not been reported till date for the complete vibrational analysis.

The present work reports a complete vibrational analysis of 2-furoic acid using IR and Raman spectra followed by normal coordinate analysis (NCA). The FTIR and FT-Raman spectra have been calculated and compared with experimental results. The DFT calculations performed at B3LYP/6-31++G* level support the wave number assignments. The redistribution of electron density (ED) in various bonding and anti-bonding orbitals and \( E \) (2) energies have also been calculated by natural bond analysis.

2 Experimental Details

The title compound 2-furoic acid was purchased from Sigma-Aldrich Chemical Company (USA). The
FTIR spectra of 2-furoic acid was recorded in the region 4000-400 cm$^{-1}$ on JASCO-6300 spectrometer with samples in the KBr. The FT-Raman spectrum of 2-furoic acid was obtained in the range 3500-50 cm$^{-1}$ using Bruker RFS 100/s FT-Raman spectrophotometer with a 1064 nm Nd:Yag laser source of 150 mW power. The spectral resolution is 2 cm$^{-1}$.

3 Computational Methods

The DFT computation of 2-furoic acid has been performed using Guassian'03 program package$^{16}$ at the Becke3-Lee-Yang-Parr(B3LYP)level with standard 6-31++G* basis set. The geometries were optimized without any constraint with the help of analytical gradient procedure implemented within Guassian 03 program. The harmonic vibrational wave numbers have been analytically calculated by taking the second derivative of energy using the simple level of theory. Multiple scaling of the force field was performed by SQM procedure$^{17,18}$ to offset the systematic errors caused by basis set incompleteness, neglect of electron correlation and vibrational anharmonicity. Normal coordinate analysis has been performed to obtain full description of the molecular motion pertaining to the normal modes with MOLVIB program version 7.0 written by Sundius$^{19,20}$. For plots of simulated IR spectra, pure Lorentizian band shapes were used with a bandwidth (FWHM) of 10 cm$^{-1}$. The Raman intensities ($S_i$) calculated by Guassian 03 program have been suitably adjusted by the scaling procedure with MOLVIB and subsequently converted to relative Raman intensities ($I_i$) using the following relationship derived from the basis theory of Raman Scattering$^{21,22}$:

$$ I_i = \frac{f(v_o - v_i)^4 S_i}{v_i \left[1 - \exp \left(\frac{-hcv_i}{kT}\right)\right]} \quad \ldots(1) $$

where $v_o$ is the exciting frequency (in cm$^{-1}$ units), $v_i$ is the vibrational wave number of the $i^{th}$ mode, $h$, $c$, $k$ are universal constants, and $f$ is the suitably chosen common scaling factor for all the peak intensities. The simulated IR and Raman spectra have been plotted using with Lorentizian shapes with full width at half maximum(FWHM) of 10 cm$^{-1}$. Natural bond orbital (NBO) analysis$^{23}$ has been performed using NBO3.1 program as implemented in the Guassian 03 W package at the DFT/B3LYP/6-31++G* level of theory.

4 Results and Discussion

4.1 Molecular geometry

The optimized molecular structure along with the numbering of atoms of 2-furoic acid is as shown in Fig. 1. The global minimum energy obtained by the DFT structure of 2-furoic acid is $-418.62478$ Hatrees. The optimized geometrical parameters are presented in Table 1.

4.2 Vibrational spectral analysis

The vibrational spectral assignments have been carried out with the help of normal coordinate analysis. The complete sets of internal coordinates of 2-furoic acid chosen according to Pulay’s recommendations$^{17}$ are presented in Table 2. The computed wave numbers have been selectively scaled according to the SQM procedure suggested by Rauhut.

![Fig. 1 — Molecular structure of 2-furoic acid with numbering of atoms](image)

Table 1 — Optimized geometrical parameters of 2-furoic acid obtained by B3LYP/6-31++G* density functional calculations

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<tr>
<th>Bond Length /Å</th>
<th>Bond Angle / °</th>
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<td>O1-C2</td>
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Table 2 — Definition of local symmetry coordinates and diagonal force constants in B3LYP/6-31++G* level for 2-furoic acid

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<thead>
<tr>
<th>Sr No</th>
<th>Symmetry Coordinates</th>
<th>Description</th>
<th>Force constants</th>
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<td>βC6H12</td>
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<td>0.70</td>
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<td>21</td>
<td>S21 = β 12,16</td>
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</table>

For numbering of atoms refer Fig. 1

Definitions are made between the valence coordinates: r_ij is the bond length between atoms i and j; β_ij is the valence angle between i,j,k where j is the central atom; γ_ijkl is the out-of-plane angle between the i-j bond and the plane defined by the j,k,l atoms; t_iijkl is the torsion (dihedral) angle between the plane defined by i,j,k and j,k,l atoms

Stretches force constants are given in mdyn Å^{-1}, bending and torsional force constants are given in mdyn Å

and Pulay. The detailed vibrational assignments of fundamental modes along with the calculated IR and Raman intensities and normal mode description (characterized by PED) are reported in Table 3. For a visual comparison, the observed and simulated FTIR and FT-Raman spectra are shown in Figs 2 and 3, respectively.

**COOH vibrations** — Vibrational analysis of carboxylic acid is made on the basis of carbonyl group and hydroxyl group. The most characteristic feature of carboxylic group is a single band observed usually in the region 1740-1660 cm\(^{-1}\) due to C=O stretching which is identical with the C=O stretch of ketones. Esters are characterized by two strong absorptions, one due to the C=O stretch vibration in the range 1750-1735 cm\(^{-1}\) and the other due to C-O Stretching near 1200 cm\(^{-1}\). In this work, the FTIR band at 1688 cm\(^{-1}\) assigned to C=O stretching vibration shows good agreement with B3LYP value at 1695 cm\(^{-1}\). The introduction of a C=C bond adjacent to a C=O bond results in a larger degree of π electron delocalization in the carbonyl and double bonds.

The lowering of C=O stretching wave number is due to the conjugation between the COOH group with the five-membered heterocyclic ring. The C-O stretching vibrations and in-plane C-OH bending vibrations are expected to be in the wide range 1450-1150 cm\(^{-1}\). Generally, C-O stretching vibrations appear at a lower
However, the PED corresponding to these vibrations are mixed modes and hence, assigning their frequencies become very difficult. For our title molecule, the frequency observed at 1424 cm\(^{-1}\) in the FTIR spectrum is assigned to C-O stretching vibration. The computed value is 1415 cm\(^{-1}\) by B3LYP method for C-O stretching vibration with a PED of 31%. The theoretically computed wavenumber at 1243 cm\(^{-1}\) is assigned to in-plane C-OH bending vibration which agrees well with the recorded spectra at 1235 cm\(^{-1}\). The PED corresponding to this vibration is 23% and is mixed with other modes as evident from Table 3.

The free hydroxyl group absorbs strongly in the region 3700-3584 cm\(^{-1}\), whereas the existence of intermolecular hydrogen bond formation can lower the O-H stretching frequency\(^{28,29}\) in the range 3500-3200 cm\(^{-1}\). The weak band at 3745 cm\(^{-1}\) in the FTIR spectrum of 2 furoic acid is due to OH stretching vibration. The theoretical calculations also predict this wave number at 3745 cm\(^{-1}\) which shows excellent agreement with the experiment value.

**C-H vibrations** — The hetero aromatic structure shows the presence of C-H stretching vibration\(^{30,31}\) in the region 3100-3000 cm\(^{-1}\). Juan Zinczuk\(^32\) has observed IR bands due to C-H stretching at 3141, 3124 and 3107 cm\(^{-1}\) in (2’-furyl)-4,5-1H-dihydroimidazole. In 2-furoic acid, the position of weak bands in FT-Raman at 3147 and 3127 cm\(^{-1}\) is due to C-H stretching vibration. The scaled values computed by B3LYP/6-31++G(d) predict C-H stretching vibration at 3145, 3139 and 3112 cm\(^{-1}\), which lie within the recorded spectral range. The PED confirms that these modes are pure stretching modes with 97%. For the furan molecule, the in-plane deformation band lies in the region 1230-970 cm\(^{-1}\). In 2 furoic acid, the in-plane C-H deformation is identified as a medium strong band at 1018 cm\(^{-1}\). Substitution patterns on the ring can be judged from the out-of-plane bending of the ring C-H bonds\(^33\) in the region 900-675 cm\(^{-1}\). The band for out-of-plane bending deformations of the title compound is identified at 847 and 738 cm\(^{-1}\). Theoretically computed frequencies for both in-plane and out-of-plane deformation vibrations by B3LYP/6-31++G(d) show excellent agreement with experimental spectrum as well as literature data\(^34,35\).

**Ring vibration** — In 2 furoic acid, the ring vibrations appear to be strongly mixed among modes as shown in Table 3. The position and intensity of these vibrations are dependent on the nature of the ring and the types of substitution. Juan Zinczuk et al\(^32\) reported C=C stretching peaks at 1549 and 1505 cm\(^{-1}\) for (2’-furyl)-4,5-1H-dihydroimidazole. In accordance with the above data, the C=C stretching vibrations computed at 1584 and 1480 cm\(^{-1}\) with PED contributions of 44% and 81% agree well with the experimental bands at 1581 and 1476 cm\(^{-1}\), respectively. The C-C stretching was observed for the furan molecule\(^32\) at 1385 cm\(^{-1}\). In this compound, the C-C stretching vibration computed by B3LYP/6-31++G(d) is at 1435 cm\(^{-1}\), while the medium strong band identified in FT-Raman spectrum at 1432 cm\(^{-1}\) is assigned to C-C stretching vibration. The FTIR bands at 1235 and 1190 cm\(^{-1}\) are associated to C-O stretching modes according to the values.
reported by Klots et al\textsuperscript{24} and Juan Zinczuk et al\textsuperscript{30}.
The DFT computations give the wave number of this band at 1243 and 1190 \text{cm}^{-1} for aromatic C-O stretching. The PED analysis identifies the C-O stretching modes with different PED values and are coupled with other modes. In this study, the observed strong FT-Raman band at 933 \text{cm}^{-1} and a weak FTIR band at 885 \text{cm}^{-1} are assigned to ring deformation which coincides well with the theoretically computed values at 932 and 858 \text{cm}^{-1}, respectively. In 2,2′-bifurane molecule, two bands of medium intensity at 613 and 596 \text{cm}^{-1} are attributed to the torsion ring modes\textsuperscript{36}. In the present work, the weak FTIR and FT-Raman bands appearing at 608 and 593 \text{cm}^{-1} belong to the torsion ring modes. These bands have been identified by the B3LYP method at 607 and 594 \text{cm}^{-1}, respectively. The PED also shows mixed contribution of approximately 65\% for these vibrations. Small changes in wavenumber observed for these modes are due to the change in force constants/reduced mass ratio resulting mainly from the extent of mixing between ring and substituent group.

5 Natural Bond Analysis
Natural bond(NBO) analysis provides an efficient method for studying intra and intermolecular bonding and interaction among bonds, and also provides a convenient basis for investigating charge transfer or conjugative interactions in molecular systems. NBO method gives useful information about interactions in both filled and virtual orbital spaces which could enhance the analysis of intra and intermolecular interactions\textsuperscript{77}. This is carried out by considering all possible interactions between filled donor and empty

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Observed wavenumbers (cm\textsuperscript{-1}) & Calculated wavenumbers(cm\textsuperscript{-1}) & A\textsubscript{IR}\textsuperscript{a} & I, R\textsuperscript{b} & Characterisation of normal modes with PED (%)\textsuperscript{c} \\
\hline
3745 & 3701 & 3745 & 98.1 & 117.3 & υOH(100) \\
- & 3147 & 3301 & 3145 & 0.1 & 153.3 & υCH(96) \\
- & 3127 & 3285 & 3130 & 0.1 & 43.5 & υCH(97) \\
 & 3268 & 3112 & 1.6 & 96.1 & υCH(97) \\
1688 & 1805 & 1696 & 471.6 & 143.9 & υC=O (30) \quad \nuCC(16)υC=C\textsubscript{ar}(16),δCO(14)υring 2(13) \\
1581 & 1611 & 1584 & 25.4 & 2.7 & \-ring 2(47)υC=\textsubscript{ar}(45) \\
1476 & 1505 & 1480 & 82.7 & 161.5 & υC=\textsubscript{ar}(80) \\
1432 & 1376 & 1415 & 54.9 & 21.7 & υC-O(31)υC=O(18)υC-\textsubscript{ar}(18) \\
1424 & 1273 & 1243 & 102.7 & 29.4 & υC-\textsubscript{ar}(34),υC-O(16)υCOH(23)υCC(17) \\
1190 & 1244 & 1190 & 0.2 & 4.6 & υC-O(36)υBC(32)υBC(15) \\
1149 & 1206 & 1148 & 138.2 & 2.8 & υC-O(35),υBC(19)υring 2(13)υBOH(11) \\
1082 & 1117 & 1094 & 218.3 & 8.1 & υC-\textsubscript{ar}(34),υC-O(16)υCOH(14),υring 2(11) \\
1076 & 1113 & 1060 & 3.9 & 11.7 & υring 2(20),υBC(20)υC=\textsubscript{ar}(19),υC-\textsubscript{ar}(18),υBC(11) \\
1018 & 1044 & 1003 & 49.5 & 2.9 & υBC(67),υC-\textsubscript{ar}(16) \\
 & 933 & 945 & 932 & 3.6 & 6.4 & υring 2(77),υC-\textsubscript{ar}(11) \\
885 & 906 & 858 & 13.2 & 7.9 & υring 1(61),υC-\textsubscript{ar}(11) \\
847 & 900 & 831 & 0.6 & 0.8 & γCH(15),γring 1(14) \\
 & 854 & 781 & 7.8 & 10.8 & δCO(44),υC-\textsubscript{ar}(31),υBOH(12) \\
738 & 774 & 760 & 42.2 & 0.6 & γCH(96) \\
677 & 722 & 691 & 40.6 & 0.4 & γCC(70)γring 2(12) \\
608 & 692 & 607 & 17.1 & 0.8 & τring 2(73)τCH(11) \\
593 & 637 & 594 & 18.9 & 1.5 & τring 1(76) \\
 & 522 & 609 & 522 & 9.4 & 0.4 & τCC(46)γCH(33) \\
 & 551 & 512 & 104.6 & 2.3 & γCH(59)τCC(24) \\
461 & 508 & 470 & 0.1 & 2.3 & βCOO(35)βCC(24)υC-\textsubscript{ar}(13) \\
437 & 415 & 433 & 1.2 & 3.2 & υC-\textsubscript{ar}(40),υring 1(15),υC-\textsubscript{ar}(15),δCO(13) \\
 & 195 & 184 & 1.9 & 0.2 & βCC(49),βCOO(45) \\
126 & 182 & 126 & 2.6 & 1.3 & γCH(94) \\
 & 88 & & & 0.0 & 0.1 & τCC(85) \\
\hline
\end{tabular}
\caption{Assignments of fundamental vibrations of 2 furoroic acid by normal coordinate analysis by SQM force field calculations using selectively scaled B3LYP/6-31+G*}
\end{table}

\textsuperscript{a}Calculated IR intensities
\textsuperscript{b}Relative Raman Intensities calculated by Eq(1) and normalized to 100
\textsuperscript{c}Only PED values greater than 10\% are given
acceptor NBOs and estimating their energy importance by second order perturbation theory. For each donor (i) and acceptor NBO(j) the stabilization energy $E(2)$ associated with electron delocalization between donor and acceptor is estimated as:

$$E(2) = \Delta E_{ij} = q^j F(i,j) / (E_j + E_i)$$

where $q^j$ is the orbital occupancy, $E_j$ and $E_i$ are diagonal elements and $F(i,j)$ is the off-diagonal NBO Fock matrix element. The larger the $E(2)$ value, the more intensive is the interaction between electron donors and electron acceptors, i.e. more donating tendency from electron donors to electron acceptors and greater the extent of conjugation of the whole system. The results of second order perturbation theory analysis of Fock matrix at B3LYP/6-31++G* level of theory are collected in Table 4. The strong intramolecular hyperconjugative interaction of the $\sigma$ and $\pi$ electrons of the C-C, C-O, C-H and O-H to the anti C-C, C-O, C-H and O-H bond of the ring as well as the COOH group leads to stabilization of some part of the ring. The intermolecular hyperconjugative interaction of the $\sigma(C2-C3)$ distribute to $\sigma^*(C2-C6)$, (C3-C4), (C3-H9), (C4-H11) leads to stabilization of approximately 2.5 KJ/mol. Further, $\pi^*(C2-C3)$ NBO conjugates with the anti-bonding orbitals of $\pi^*(C4-C5)$ and (C6-C7) which lead to strong delocalization of 15.08 and 22.38 KJ/mol, respectively. The same kind of interaction was calculated in the bond for (C4-C5) which is shown in Table 5. The $\pi^*(C6-C7)$ of the NBO conjugated with the $\pi^*(C5-C6)$ results in an enormous stabilization of 173.55 KJ/mol.

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<tr>
<th>Donor (i)</th>
<th>ED (i) (e)</th>
<th>Acceptor (j)</th>
<th>ED (j) (e)</th>
<th>$E(2)^a$ (KJmol$^{-1}$)</th>
<th>$E(j)-E(i)^b$ (a.u)</th>
<th>$F(i,j)^c$ (a.u)</th>
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<td>3.65</td>
<td>1.21</td>
<td>0.059</td>
<td></td>
</tr>
</tbody>
</table>

$^aE(2)$ means energy of hyper conjugative interactions

$^b$Energy difference between donor and acceptor i and j NBO orbitals

$^cF(i,j)$ is the Fock matrix element between i and j NBO orbitals
The most important interactions related to the resonance in the molecule are electron donation from the lone pairs of O1, O7 and O8 to the σ and π antibonding orbitals. The occupancy of sp-hybrid lone pair orbitals of n1(O1), n1(O7) and n1(O8) are relatively high (1.97, 1.98 and 1.98e), respectively while that of the second lone pair orbital of n2(O1), n2(O7) and n2(O8) is considerably low (1.68, 1.84, 1.83e), respectively indicating that the latter orbital is extensively involved in charge donation which is evident in Table 4. The charge transfer from the n2(O1) of the ring hetero atom to the π*(C2-C3) and π*(C4-C3) (stabilization energy of 27.30 and 30.21 kJ/mol) is a measure of delocalization within the furan ring. NBO analysis shows true delocalization effects in the hyper conjugative interaction n2(O7)→σ*(C6-O8) of the compound studied (stabilization energy of 33.96 kJ/mol). The magnitude of charges transferred from the lone pair of n2(O7) into the anti-bond σ*(C6-O8) increases the electron density in the respective bond to 0.103e yielding to the weakening of (C6-O8) sigma bond. The interaction between lone pair orbital n2 (O8) with that of anti-bonding π(C6-O7) whose charge transfer energy value is 44.68 kJ/mol denotes larger delocalization.

6 Conclusions

Complete vibrational analysis of 2-furoic acid has been performed on the basis of DFT calculations at the B3LYP/6-31+G* levels of theory. The role of carboxylic group in the vibrational frequencies of 2-furoic acid has been studied. The assignments of wave numbers of 2-furoic acid are quite comparable indicating that the former orbital is extensively involved in charge donation which is evident in Table 4. The charge transfer from the n2(O1) of the ring hetero atom to the π*(C2-C3) and π*(C4-C3) (stabilization energy of 27.30 and 30.21 kJ/mol) is a measure of delocalization within the furan ring. NBO analysis shows true delocalization effects in the hyper conjugative interaction n2(O7)→σ*(C6-O8) of the compound studied (stabilization energy of 33.96 kJ/mol). The magnitude of charges transferred from the lone pair of n2(O7) into the anti-bond σ*(C6-O8) increases the electron density in the respective bond to 0.103e yielding to the weakening of (C6-O8) sigma bond. The interaction between lone pair orbital n2 (O8) with that of anti-bonding π(C6-O7) whose charge transfer energy value is 44.68 kJ/mol denotes larger delocalization.

References
