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FT-Raman, FT-IR spectra and DFT calculations on monomeric and dimeric structures of 5-fluoro- and 5-chloro-salicylic acid

Mehmet Karabacak,[a]* Etem Kose[a] and Mustafa Kurt[b]

The experimental and theoretical study on the structures and vibrations of 5-fluoro-salicylic acid and 5-chloro-salicylic acid (5-FSA and 5-ClSA, $C_7H_5FO_3$ and $C_7H_5ClO_3$) is presented. The Fourier transform infrared spectra (4000–400 cm^{-1}) and the Fourier transform Raman spectra (4000–50 cm^{-1}) of the title molecules in the solid phase were recorded. The molecular structures, vibrational wavenumbers, infrared intensities, Raman intensities and Raman scattering activities were calculated for a pair of molecules linked by the intermolecular O–H···O hydrogen bond. The geometrical parameters and energies of 5-FSA and 5ClSA were obtained for all eight conformers/isomers from density functional theory (DFT) (B3LYP) with 6-311++G(d,p) basis set calculations. The computational results identified the most stable conformer of 5-FSA and 5-ClSA as the C1 form. The complete assignments were performed on the basis of the total energy distribution (TED) of the vibrational modes, calculated with scaled quantum mechanics (SQM) method. The spectroscopic and theoretical results were compared with the corresponding properties for 5-FSA and 5-ClSA monomers and dimer of C1 conformer. The optimized bond lengths, bond angles and calculated wavenumbers showed the best agreement with the experimental results. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: 5-fluoro-salicylic acid; 5-chloro-salicylic acid; IR and Raman spectra; DFT; intermolecular hydrogen bond

Introduction

Salicylic acid (also known as 2-hydroxybenzoic acid) is the simplest aromatic carboxylic acid; it contains both a hydroxyl group and a carboxyl group. It is widely used in the food industry as a plant growth regulator, as an ingredient in antimicrobial washes to inhibit the spoilage of fresh vegetables and as a preservative in food products (antimicrobial and antifungal agent).[1,3] It has recently become attractive to experimentalists because of biological significance, particularly in medicinal and enzyme chemistry.[4–7]

Salicylic acid and its derivatives could present as a good model system for researching H-bonding and the effect of additional hydroxyl substitution in aromatic moieties. Extensive experimental and theoretical investigations have focused on elucidating the structures and normal vibrations of salicylic acid and its derivatives.[4,5,8–26] Experimentally, Raman spectra of salicylic acid were reported.[8,9] Salicylic acid and its derivates with FT-IR and NMR spectra were obtained and the substituent effect on the spectral properties of salicylic acid derivatives was investigated by Jadrijević et al.[10] Yahagi et al.[11] measured vibrational spectra of jet-cooled salicylic acid. Volvo et al.[12] calculated normal coordinates for salicylic acid molecule and proposed the assignment of the observed Raman and IR spectra. Aqueous solutions of salicylic acid and its derivatives in various pH were investigated using infrared and Raman spectra by Humbert et al.[13] The crystal structure of salicylic acid has been studied by X-ray.[14,15] We have also published an experimental and theoretical study on structure and vibrations of 5-bromo-salicylic acid.[16] Plánka et al.[17] studied the copper (II)-5-fluoro-salicylic acid system in water and 50 v/v% water–methanol mixture by pH potentiometry combined with UV–VIS spectrophotometer, and by the two-dimensional electron spin resonance (ESR) simulation

method, respectively. Influence of particle size on the quantitative determination of salicylic acid in a pharmaceutical ointment using FT-Raman spectroscopy was studied by De Beer et al.[18] Han et al.[19] investigated the inhibitory effects of 4-chloro-salicylic acid on the activity of mushroom tyrosinase. The quantitative characterization of acetylsalicylic in various pharmaceutical compounds was reported by Bunaciu et al.[20] Goulet and Aroca[21] presented the infrared and Raman spectra of solid salicylic acid and performed DFT/B3LYP/6-311+G(d,p) calculations.

Boczar et al.[22] presented theoretically quantitative description of infrared spectra in the O–H stretching region of hydrogen-bonded salicylic acid. Chen and Shyu[23] investigated conformers and intramolecular hydrogen bonding of salicylic acid monomer and its anions. An experimental and theoretical study on amino-substituted salicylic acid was reported.[4] The molecular structures and the intramolecular hydrogen bonding for salicylic acid, 2-hydroxythiobenzoic acid, 2-hydroxythionobenzoic acid and 2-hydroxydithiobenzoic acid have been precisely investigated using an ab initio and DFT methods.[24] Infrared and Raman spectra, ab initio calculations and vibrational assignment of 4-amino-salicylic acid were studied by Akkaya and Akyüz.[25] They obtained seven stable conformers for 4-amino-salicylic acid. Nogueria[26] investigated the wavenumbers of 3-amino-salicylic acid and 2-mercaptonicotinic acid by using infrared and Raman spectra.

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The geometric structures of 5-fluoro-salicylic acid and 5-chloro-salicylic acid (5-FSA and 5-ClSA) with caffeine complex are studied by X-ray.[27,28] However, literature survey reveals that, to the best of our knowledge, no experimental and computational vibrational spectroscopic study on free 5-FSA and 5-ClSA has been published so far. This inadequacy observed in the literature encouraged us to make this theoretical and experimental vibrational spectroscopic research based on the conformers of molecule to give a correct assignment of the fundamental bands in experimental FT-IR and FT-Raman spectra. Therefore, the present study aims to give a complete description of the molecular geometry and molecular vibrations of the 5-FSA and 5-ClSA.

5-FSA and 5-ClSA (also known as 5-flouro-2-hydroxybenzoic acid and 5-chloro-2-hydroxybenzoic acid) are substituted benzene with three different functional groups; an OH, an F or Cl atom and a COOH group. A model system, salicylic acid and flouro (or chloro) parts are chosen as an example of hydrogen-bonded system with two types of hydrogen bonds: inter-(HO···HOOC) and intramolecular (i.e. intra-COOH). The possible stable conformers of 5-FSA and 5-ClSA molecules were searched. There are eight conformers for 5-FSA and 5-ClSA. The optimized geometry and vibrational wavenumbers for conformers of 5-FSA and 5-ClSA were calculated at DFT/B3LYP level of theory using the 6-311++G(d,p) basis set. The C1 form is the more stable conformer than the others for the title molecules. The results of the theoretical and spectroscopic studies are reported herein. Detailed interpretations of the vibrational spectra of 5-FSA and 5-ClSA have been made on the basis of the calculated total energy distribution (TED).

Experimental

The compounds 5-FSA and 5-ClSA samples in solid state were purchased from Acros Organics Company with a purity of 99%, and they were used as obtained without further purification. The samples were prepared using a KBr disc technique because of solid states. The spectra of molecules (5-FSA and 5ClSA) were recorded in the region 400–4000 cm^{-1} on a Perkin Elmer FT-IR System Spectrum BX spectrometer calibrated using polystyrene bands. FT-Raman spectra of the samples were recorded using 1064-nm line of an Nd : YAG laser as excitation wavelength in the region 50–4000 cm^{-1} on a Bruker RFS 100/S FT-Raman spectrometer. The detector was a liquid nitrogen cooled Ge detector. Five hundred scans were accumulated at 4 cm^{-1} resolution using a laser power of 100 mW.

Computational Details

The geometry data of 5-FSA and 5-ClSA (with Caffeine complex) molecules were taken from X-ray structure.[27,28] In order to obtain stable structures, the geometrical parameters for eight conformers/isomers and dimer structure of title molecules in the ground state (*in vacuo*) were optimized at DFT/B3LYP level of theory using the 6-311++G(d,p) basis set. The vibrational wavenumbers of the compound dimer with H-bonding between carboxyl groups of C1 conformation/isomer have also been calculated to improve the simulation of the experimental spectra for each molecule. The vibrational wavenumbers for the eight conformers are calculated with this method and then wavenumbers in the ranges from 4000 to 1700 cm^{-1} and lower than 1700 cm^{-1} are scaled with 0.958 and 0.983, respectively.[29]

The theoretical results have enabled us to make the detailed assignments of the experimental IR and Raman spectra of title molecules. The TED of the molecules was calculated by using the scaled quantum mechanics (SQM)[30] program, and the fundamental vibrational modes were characterized by their TED. We tabulated C1 conformer and dimer calculations data because of most stable conformer for 5-FSA and 5-ClSA. All the calculations were performed by using the Gaussview molecular visualization program and the *Gaussian03* program package on the personal computer.[31] The Becke's three-parameter hybrid density functional, B3LYP,[32,33] was used to estimate harmonic vibrational wavenumbers with the 6-311++G(d,p) basis set. It is well known in the quantum chemical literature that among the available functionals, the B3LYP functional yields a good description of harmonic vibrational wavenumbers for small- and medium-sized molecules.

The Raman activities (S_{Ra}) calculated with Gaussian03 program[31] are converted to relative Raman intensities (I_{Ra}) using the following relationship derived from the intensity theory of Raman scattering[34,35]

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

where ν_0 is the laser exciting wavenumber in cm^{-1} (in this work, we have used the excitation wavenumber $\nu_0 = 9398.5$ cm^{-1}, which corresponds to the wavelength of 1064 nm of an Nd : YAG laser), ν_i 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 K, respectively.

Results and Discussion

The molecules of 5-FSA and 5-ClSA have three substituents such that the fluoro atom(or the chloro atom), hydroxyl group(OH) and carboxyl group (COOH) attached to a planar benzene ring. All forms of molecules, hydroxyl group, carboxyl group and benzene ring are in the same plane. All conformers of title molecules and C1 dimer forms which contain two intermolecular and two intramolecular hydrogen bonds are shown in Figs 1 and 2.

Energetics

Calculated energies and energy difference [the relative energy of the other conformers was as: $\Delta E = E(Cn) - E(C1)$, the conformer C1 is the lowest energy as reference point] for all conformers of 5-FSA and 5-ClSA molecules determined by DFT/B3LYP/6-311++G(d,p) are presented in Table 1. Intra-hydrogen bonds can be responsible for the geometry and the stability of a predominant conformation; the formation of hydrogen bonding between a hydroxyl group and O=COH cause the structure of the conformer C1 to be the most stable conformer for 5-FSA and 5-ClSA. Additionally, the calculations showed that the conformer C8 to be the least stable conformer as shown in Table 1. From DFT calculations of conformers with 6-311++G(d,p) basis set, the conformer C1 is predicted more stable from 0.0054 to 0.0393 and from 0.0055 to 0.0397 kcal mol^{-1} than the other conformers of 5-FSA and 5-ClSA molecules, respectively. C1 and C2 conformers are
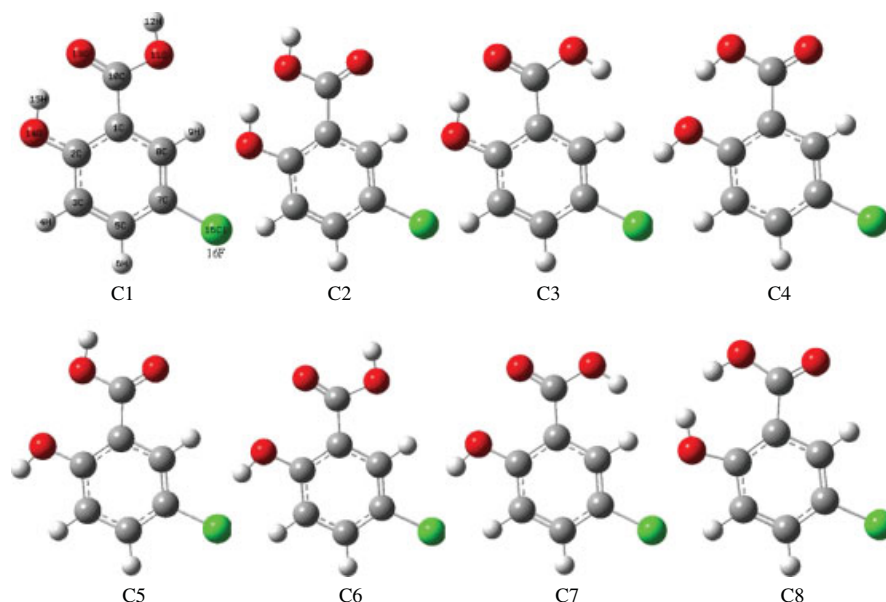
Figure 1. The theoretical geometric structures of 5-FSA and 5-ClSA molecules.
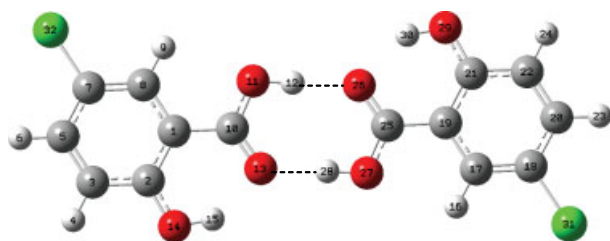

Figure 2. C1 dimer conformer of 5-FSA and 5-ClSA molecules.

calculated to have lower energies than the other conformers even though threre might exist weaker hydrogen bonding either between the O–H group and the O atom with COOH group or between the H atoms with COOH group and the O–H group for 5-FSA and 5-ClSA molecules.

Geometrical structures

The molecular structure of 5-FSA and 5-ClSA with caffeine complex has been studied by X-ray diffraction.[27,28] However, a literature survey reveals that to the best of our knowledge, no experimental geometric structure study on free 5-ClSA and its dimer structure are published yet. For 5-ClSA, we compare calculated results with 5-ClSA structure. The first task for the computational work was to determine the optimized geometry for each molecule. The atomic numbering scheme of the most stable conformer, other conformers and dimer structure of the title samples are shown in Figs 1 and 2.

The predicted bond lengths and bond angles for the most stable conformer (C1) and dimer of C1 conformers of molecules are tabulated in Table 2 in comparison to the experimental values. Taking into account that the molecular geometry in the vapor phase may be different from the solid phase, owing to extended hydrogen bonding and stacking interactions there is reasonable agreement between the calculated and experimental geometric parameters. By comparing the calculated and observed bond lengths, the theoretical parameters are generally bigger than experimental data.

Several authors[36,37] have explained the changes in wavenumber or bond length of the C–H bond on substitution due to a change in the charge distribution on the carbon atom of the

Table 1. Calculated energies and energy difference for eight conformers of 5-FSA and 5-ClSA with DFT [B3LYP/6-311++G(d,p)] method

	5-FSA			5-ClSA		
Conformers	Energy (hartree)	Energy (kcal mol^{-1})	Energy differences (kcal mol^{-1})[a]	Energy (hartree)	Energy (kcal mol^{-1})	Energy differences (kcal mol^{-1})[a]
C1	−595.47134254	−373663.9244	0.0000	−955.82643789	−599790.1701	0.0000
C2	−595.46590513	−373660.5124	0.0054	−955.82090513	−599786.6983	0.0055
C3	−595.46019390	−373656.9285	0.0111	−955.81534838	−599783.2114	0.0111
C4	−595.45570349	−373654.1108	0.0156	−955.81038221	−599780.095	0.0161
C5	−595.45428484	−373653.2206	0.0171	−955.80928209	−599779.4047	0.0172
C6	−595.45369165	−373652.8483	0.0177	−955.80873362	−599779.0605	0.0177
C7	−595.43967295	−373644.0515	0.0317	−955.79478994	−599770.3107	0.0316
C8	−595.43201298	−373639.2447	0.0393	−955.78678156	−599765.2854	0.0397

[a] Energies of the other seven conformers relative to the most stable C1 conformer.

Table 2. Comparison of geometric parameters for the monomer and dimer C1 conformers of 5-FSA and 5-ClSA (bond lengths in angstrom and bond angles in degrees)

Parameters Bond lengths (Å)	5-FSA			5-ClSA		
	X-ray[27]	Monomer	Dimer	X-ray[28]	Monomer	Dimer
C1–C2	1.402	1.416	1.416	1.412	1.416	1.416
C1–C8	1.400	1.408	1.409	1.408	1.407	1.409
C1–C10	1.467	1.466	1.465	1.474	1.467	1.466
C2–C3	1.386	1.403	1.403	1.399	1.402	1.402
C2–O14	1.352	1.344	1.344	1.347	1.342	1.342
C3–H4	0.930	1.083	1.083	1.430	1.083	1.083
C3–C5	1.366	1.384	1.383	1.369	1.383	1.383
C5–H6	0.940	1.083	1.083	0.940	1.083	1.083
C5–C7	1.372	1.394	1.394	1.424	1.400	1.400
C7–C8	1.357	1.374	1.373	1.370	1.379	1.379
C7–X16	1.357	1.357	1.356	1.756	1.758	1.758
C8–H9	0.910	1.081	1.081	0.910	1.081	1.081
C10–O11	1.308	1.347	1.317	1.316	1.347	1.316
C10–O13	1.225	1.225	1.246	1.238	1.225	1.246
O11–H12	0.950	0.969	0.998	0.960	0.969	0.998
O13–H15	1.830	1.767	1.766	1.828	1.763	1.763
O14–H15	0.870	0.981	0.979	0.840	0.981	0.979
Bond angles (°)						
C2–C1–C8	119.3	119.8	119.7	119.4	119.8	119.6
C2–C1–C10	120.0	119.0	120.1	121.4	118.9	120.0
C8–C1–C10	120.7	121.2	120.3	119.2	121.3	120.3
C1–C2–C3	119.2	119.2	119.2	120.1	119.0	119.1
C1–C2–O14	123.4	123.2	123.5	122.6	123.2	123.5
C3–C2–O14	117.4	117.6	117.4	117.3	117.7	117.5
C2–C3–H4	119.0	118.3	118.3	112.0	118.4	118.3
C2–C3–C5	121.0	120.6	120.6	119.8	120.6	120.7
H4–C3–C5	120.0	121.1	121.1	128.0	121.0	121.0
C3–C5–H6	122.2	121.1	121.1	122.0	120.2	120.2
C3–C5–C7	119.0	119.4	119.4	120.7	120.0	120.0
H6–C5–C7	118.7	119.5	119.5	117.0	119.7	119.8
C5–C7–C8	122.4	121.9	121.8	119.8	120.6	120.6
C5–C7–X16	118.7	118.7	118.7	120.5	119.4	119.4
C8–C7–X16	118.9	119.4	119.5	119.7	120.0	120.0
C1–C8–C7	119.1	119.2	119.3	120.3	119.9	120.0
C1–C8–H9	119.2	120.4	120.2	122.0	119.4	119.2
C7–C8–H9	121.8	120.4	120.5	117.0	120.7	120.8
C1–C10–O11	115.4	114.6	115.8	114.9	114.7	118.9
C1–C10–O13	122.2	124.3	122.0	122.6	124.2	118.9
O11–C10–O13	122.4	121.1	122.1	122.6	121.1	122.1
C10–O11–H12	110.7	107.1	110.6	110.0	107.2	110.6
C2–O14–H15	106.0	108.1	108.0	106.0	108.1	108.0
Intermolecular H bond lengths and angles						
H12···O26 (H28···O13)	1.723		1.676			1.677
O13···O27 (O11···O26)	2.676		2.674			2.674
O11–H12···O26	177.2		179.6			179.7
O27–H28···O13	177.2		179.6			179.7

X: F or Cl atom.

benzene ring. The substituents may be either of the electron withdrawing type (F, Cl, and Br, ...).[16] The carbon atoms are bonded to the hydrogen atoms with a σ bond in benzene, and the substitution of a halogen for hydrogen reduces the electron density at the ring carbon atom. The ring carbon atoms in substituted benzenes exert a larger attraction on the valence electron cloud of the hydrogen atom resulting in an increase in the C–H force constant and a decrease in the corresponding bond length. The reverse holds well on substitution with electron donating groups. The serious revision in the C–H bond length could be affected by the combined effects of the inductive–mesomeric interaction and the electric dipole field of the polar substituents.[16]

The estimation of the C–H bond lengths by X-ray is intrinsically inaccurate because of the low-electronic density on the hydrogen atom.[27,28] The perceivable ones are for the bond distances of C–H among which the biggest difference is 0.171 Å. For example, these bond lengths were found to be in the range of 0.910–0.940 Å in 5-FSA crystal,[27] but theoretically calculated values are greater than 1 Å for 5-FSA.

The C–X (X: F, Cl, Br, ...) bond length indicates a considerable increase when substituted in place of C–H, in other word, the bond length increases from C–F to C–Br. This has been observed even in benzene derivatives.[38] Atoms F and Cl are in the plane of the salicylic acid. The calculated bond distance value of C–F and C–Cl is in good agreement with the experimental value (Table 2). In International Tables for Crystallography,[39] the CO bond lengths in the carboxylic acid group conform to the average values that are tabulated for an aromatic carboxylic acid in which C=O is 1.226 Å and C–O is 1.305 Å. The corresponding bond lengths in 5-FSA are 1.225 Å (C=O) and 1.308 Å (C–O).[27] In 5-ClSA, these values are 1.238 Å and 1.316 Å respectively.[28] They are calculated 1.225 Å (C=O) and 1.347 Å (C–O) for 5-FSA and 1.225 Å and 1.347 Å for 5-ClSA.

The bond lengths are found to be similar for two molecules (5-FSA, 5-ClSA) which are in good agreement with experimental values.[27,28] We can also enounce most of the bond angles and distances are almost the same for all conformers but there are some differences that should be mentioned for title samples. However, there are small differences the other conformations that should be touched on. This one is C=O bonds of molecules which compared with all conformers, C1 conformer's data are approximate the experimental data. C1 conformer of 5-ClSA has the C10–O13 bond distance 1.238 Å, this band obtained 1.225 Å with X-ray.[28] But the C10–O13 calculated bond distance of 5-FSA is coincident with X-ray.[27] The bond distance C1–C10 among C1 conformers of 5-FSA and 5-ClSA are smaller than the other conformers. This bond was found to be 1.467 Å in 5-FSA[27] crystal, 1.474 Å in 5-ClSA[28] and calculated as the biggest in unstable conformer C8 of 5-FSA and 5-ClSA (1.512 Å and 1.512 Å) probably due to the effect of intra-hydrogen (H16···O14) on the structure.

In the ring part, the optimized geometry of the molecules shows very good agreement with experiment. The CC bond lengths of the benzene rings of 5-FSA and 5-ClSA are observed in the range

of 1.357–1.402 Å[27] and 1.369–1.412 Å[28] which calculated in the range 1.374–1.416 Å and 1.379–1.416 Å, respectively. For salicylic acid, these bond lengths are observed in the range of 1.383–1.416 Å.[40] The similar correlation was found for similar molecules in the literature.[16,24,25]

The asymmetry of the benzene ring is also evident from the negative and positive deviation from the normal value of 120°. C2–C1–C10 angle is smaller than C8–C1–C10 because of interaction between the carboxyl acid (COOH) and hydroxyl (OH) group for title molecules. These results also are obtained for 5-BrSA.[16]

The geometric dimer structure of 5-FSA is studied by X-ray.[27] But, no experimental geometric dimer structure of 5-ClSA is published in the literature yet. Therefore, we could not compare the calculation results for 5-ClSA dimer structure with the experimental data. For 5-FSA, the intermolecular hydrogen bonds are almost linear (the O–H···O angle equals 177.0°) and their length is 2.676 Å.[27] We calculated this angle and at length 179.6° and 2.674 Å. The intramolecular hydrogen bonds between the hydroxyl groups and the oxygen atoms of the carbonyl groups are strongly bent (the O–H···O angle equals 149.0°) and the O···O distance is 2.615 Å. The calculated values (144.3° and 2.624 Å) are good agreement with experimental values. Hydrogen bonds with the intermolecular are also linear (the O–H···O angle equals 179.0°) and their length is 2.636 Å and the intramolecular hydrogen bonds are strongly bent (the O–H···O angle equals 145.4°) and the O···O distance is 2.608 Å for salicylic acid.[22]

Vibrational spectra

In order to obtain the spectroscopic signature of 5-FSA and 5-ClSA molecules, we performed a wavenumber calculation analysis. Calculations were made for free molecules in vacuum, while experiments were performed for solid samples; so there are disagreements between calculated and observed vibrational wavenumbers, and some wavenumbers are calculated. However, these wavenumbers are not observed in the FT-IR and FT-Raman spectra.

Both these molecules consists of 16 atoms, so they have 42 normal vibrational modes. On the basis of C_s symmetry, the 42 fundamental vibrations of 8 forms of the title molecule can be distributed as 29A′ + 13A″. The vibrations of the A′ species are in plane and those of the A″ species are out of plane. But if the molecules were of C_1 symmetry, there would not be any relevant

Table 3. Comparison of the experimental (FT-IR and FT-Raman) wavenumbers (cm^{-1}) and theoretical harmonic wavenumbers (cm^{-1}), of C1 monomer and dimer conformer of 5-FSA calculated by B3LYP method using 6-311++G(d,p) basis set

Modes no	Symmetry species	Experimental		Theoretical C1 monomer conformer		Theoretical C1 dimer conformer		TED (≥10%)
		FT-IR	FT-Raman	Unscaled wavenumbers	Scaled wavenumbers	Unscaled wavenumbers	Scaled wavenumbers	
ν1	A′			3768	3609	3234, 3150	3098, 3018	νOH (100) (O11–H12)
ν2	A′	3244		3485	3339	3523, 3522	3375, 3374	νOH (100) (O14–H15)
ν3	A′	3090	3087	3223	3088	3224, 3224	3089, 3089	νCH (100)
ν4	A′	3074		3207	3072	3208, 3207	3073, 3072	νCH (100) symmetric
ν5	A′			3194	3059	3194, 3194	3060, 3060	νCH (100) asymmetric
ν6	A′	1670	1660	1732	1660	1697, 1681	1668, 1652	νC=O (78)
ν7	A′	1628		1664	1636	1659, 1639	1631, 1611	νCC (63) ring + νC=O (10)
ν8	A′	1591	1592	1624	1596	1623, 1619	1595, 1591	νCC (62) ring + δCCH (12) + δCOH (10)
ν9	A′	1483	1480	1514	1488	1518, 1512	1492, 1486	δCCH (42) + νCC (30) ring
ν10	A′	1443	1446	1471	1446	1468, 1456	1443, 1431	νCC (44) + δCOH (21) + νCO (12)

Table 3. (Continued)

Modes no	Symmetry species	Experimental		Theoretical C1 monomer conformer		Theoretical C1 dimer conformer		TED (≥10%)
		FT-IR	FT-Raman	Unscaled wavenumbers	Scaled wavenumbers	Unscaled wavenumbers	Scaled wavenumbers	
$\nu 11$	A′	1385		1419	1395	1493, 1477	1468, 1452	δCOH (39) + νCC (23) + νCO (15) + δCCO (10)
$\nu 12$	A′	1329		1392	1368	1400, 1399	1376, 1375	νCC (50) ring + δCOH (15)
$\nu 13$	A′	1299	1326	1324	1302	1324, 1321	1301, 1299	δCCH (30) + νCO (26) + νCC (20) + δCOH (12)
$\nu 14$	A′	1254	1274	1293	1271	1272, 1269	1250, 1247	νCC (37) ring + νCO (27) + νCF (20) + δCOH (15)
$\nu 15$	A′	1222	1245	1261	1240	1254, 1249	1233, 1228	δCCH (32) + νCF (20) + νCC (10) + δCOH (13)
$\nu 16$	A′	1204	1181	1215	1194	1211, 1210	1190, 1189	δCCH (29) + νCC (25) + νCF(15) + δCOH (12)
$\nu 17$	A′			1177	1157	1365, 1354	1342, 1331	δCOH (42) + δCCH (15) + νCO(24) + νCF(10)
$\nu 18$	A′	1122	1122	1143	1123	1147, 1146	1128, 1127	δCCH (61) + δCCC (19)
$\nu 19$	A′	1068	1067	1078	1060	1096, 1094	1077, 1075	νCC(25) + δCCH (25) + νCO (24) + δCCC (10)
$\nu 20$	A″	958	942	964	948	969, 969	953, 953	γC−H (90)
$\nu 21$	A′	940		950	934	956, 956	940, 940	νCC(35) + νCF (17) + νC−COOH(13) + δCCC(10)
$\nu 22$	A″	881		899	883	904, 904	889, 889	γC−H (89)
$\nu 23$	A″	822		841	827	845, 841	831, 827	γC−H (85)
$\nu 24$	A′	794	794	804	790	811, 808	797, 794	δCCC(35) trigonal ring breath + νCO(22) + νCF(10)
$\nu 25$	A″	761		786	773	790, 784	777, 771	τCCCO (58) + γOH (30) (O11−H12)
$\nu 26$	A″		744	732	720	711, 709	699, 697	γOH (97) (O14−H15)
$\nu 27$	A′			732	720	769, 754	756, 741	δCCC (22) + νCC (20) + δCCC (16) + νCO (10)
$\nu 28$	A″	676	670	684	672	696, 696	684, 684	τCCCC (65) + τOCOH (14) + τOCCC (10)
$\nu 29$	A′			671	659	689, 685	677, 673	δOCC (29) + δOCO (25) + δCCC (19)
$\nu 30$	A″	564		575	566	934, 848	918, 834	γOH (80) (O11−H12) + τCCCO (10)
$\nu 31$	A′	538	553	551	542	571, 564	561, 554	δCCO (50) + δCCC (12) + δOCO (12) + δCCF(10)
$\nu 32$	A″			540	531	550, 550	541, 541	τCCCH (31) + τCCCC (23) + τCCOH (19)
$\nu 33$	A′	467	472	470	462	473, 470	465, 462	δCCC (45) ring + νCF (13) + νCC (10)
$\nu 34$	A′	437	451	440	433	479, 460	471, 452	δCCO (56) + νCC (15) + δCCC (10) ring
$\nu 35$	A″			431	424	442, 441	434, 434	τCCCC (55) + τCCOH (15) + τCCCC (10)
$\nu 36$	A′		402	397	390	408, 407	401, 400	δCCF (41) + δCCO (30) + δCCC (10)
$\nu 37$	A″		377	370	363	372, 371	366, 365	τCCCF (45) + τCCCO (31) + τCCCH (12)
$\nu 38$	A′		248	348	342	370, 354	364, 348	δCCO (31) + δCCC (20) + δCCF (18) + νCC (13)
$\nu 39$	A′		197	213	209	260, 251	256, 247	δC−COOH (78) + δCCF (12)
$\nu 40$	A″		161	169	166	179, 172	176, 169	τCCCO (40) + τCCCF (25) + τCCCC (10)
$\nu 41$	A″			139	136	142, 138	140, 136	τC−COOH (44) + τCCCC (35)
$\nu 42$	A″		84	86	84	89, 77	87, 76	tCOOH (89)
σ (rms)				64.637	21.989			
R^2				0.9992	0.9994			

ν; stretching, δ; in-plane bending, γ; out-of-plane bending, τ; torsion, t; twisting.

Table 4. Comparison of the experimental (FT-IR and FT-Raman) wavenumbers (cm^{-1}) and theoretical harmonic wavenumbers (cm^{-1}) of C1 monomer and dimer conformer of 5-ClSA calculated by B3LYP method using 6-311++G(d,p) basis set

Modes no	Symmetry species	Experimental		Theoretical C1 monomer conformer		Theoretical C1 dimer conformer		TED ($\geq$10%)
		FT-IR	FT-Raman	Unscaled wavenumbers	Scaled wavenumbers	Unscaled wavenumbers	Scaled wavenumbers	
ν1	A'	3546		3767	3608	3234, 3151	3098, 3019	νOH (100) (O11−H12)
ν2	A'	3233		3476	3330	3515, 3514	3367, 3366	νOH (100) (O14−H15)
ν3	A'	3085		3222	3086	3223, 3223	3088, 3088	νCH (100)
ν4	A'	3064	3073	3206	3072	3207, 3207	3072, 3072	νCH (100) symmetric
ν5	A'	2910		3193	3059	3193, 3193	3059, 3059	νCH (100) asymmetric
ν6	A'	1675	1648	1732	1660	1694, 1672	1665, 1644	νC=O (78)
ν7	A'	1610		1647	1619	1642, 1626	1614, 1598	νCC (60) ring + νC=O (10)
ν8	A'	1576	1575	1610	1583	1610, 1606	1583, 1579	νCC (60) ring + δCOH (14) + δCCH (10)
ν9	A'	1473	1474	1503	1477	1510, 1501	1484, 1475	δCCH (47) + νCC (17) ring
ν10	A'	1443	1430	1454	1429	1449, 1440	1424, 1416	νCC (43) + δCOH (24) + νCO (11)
ν11	A'		1413	1418	1393	1487, 1476	1462, 1451	δCOH (35) + νCC (25) + νCO (14) + δCCO (10)
ν12	A'	1361		1387	1363	1397, 1395	1373, 1371	νCC (42) ring + δCOH (18)+ δCCH (12)
ν13	A'	1318	1316	1328	1305	1359, 1353	1336, 1330	δCCH (34) + νCC (26) ring + νCO (25)
ν14	A'	1292	1295	1294	1272	1327, 1325	1304, 1302	νCC (35) ring + νCO (27) + δCOH (14)
ν15	A'	1228	1224	1248	1227	1246, 1244	1225, 1223	δCCH (47) + νCC (22) ring + δCOH (18)
ν16	A'	1200		1190	1170	1263, 1262	1242, 1241	δCOH (39) + νCC (32) + νCO (10)
ν17	A'	1129	1154	1162	1143	1171, 1170	1151, 1150	δCCH (52) + νCC (23) ring + νCO (10)
ν18	A'	1106	1106	1115	1096	1124, 1125	1105, 1106	δCCC (40) + νCC (35) trigonal ring breat + νCCl (15)
ν19	A'	1081	1081	1086	1068	1098, 1098	1079, 1079	δCCH (32) + νCC (30) + νCO (22)
ν20	A''	954		973	957	978, 978	961, 961	γC−H (89)
ν21	A''	890		910	894	915, 915	899, 899	γC−H (87)
ν22	A'	880	882	887	872	895, 893	880, 878	δCCC (41) + νCO (15) + νCC (14) + νCCl (11)
ν23	A''	826		840	826	844, 844	830, 830	γC−H (90)
ν24	A''	786	782	786	773	792, 787	779, 774	τCCCO (57) + τOCOH (25)
ν25	A'	758		781	768	806, 796	792, 782	νCC (45) + νCO (17) trigonal ring breat + δCOC (10)
ν26	A''	704		737	725	717, 715	705, 703	γOH (96) (O14−H15)
ν27	A''	678	687	691	679	699, 699	687, 687	τCCCC (70) + τOCOH (14)
ν28	A'			679	667	712, 701	700, 689	δOCO (57) + δCCO (18) + νCCl (13) + νCO (10)
ν29	A'	651	649	656	645	659, 659	648, 648	δCCC (45) + νCCl (25)
ν30	A''	554		574	564	937, 860	921, 845	γOH (80) (O11−H12)
ν31	A'		547	543	534	565, 558	555, 549	δCCO (50) + δCCC (13) + δOCO (11)
ν32	A''	529		538	529	540, 540	531, 531	τCCCH(32)+ τCCCC(25) + τCCOH (15) + τCCCO(10)
ν33	A'	464	450	443	435	476, 460	468, 452	δCCO (58) + δCCC (14) + νCC (12)
ν34	A''	429		425	418	443, 442	435, 434	τCCCC (55) + τCCCO (19) + τCCCH (15)
ν35	A'		392	380	374	400, 385	393, 378	νCCl (27) + νC−COOH (23) + δCCC (20)
ν36	A'		369	366	360	377, 369	371, 363	δCCC (34) + νCCl (30) + δCCO (20)

Table 4. (Continued)

Modes no	Symmetry species	Experimental		Theoretical C1 monomer conformer		Theoretical C1 dimer conformer		TED ($\geq$10%)
		FT-IR	FT-Raman	Unscaled wavenumbers	Scaled wavenumbers	Unscaled wavenumbers	Scaled wavenumbers	
$\nu37$	A″		338	331	326	334, 333	328, 327	τCCCCl (40) + τCCCO (33) + τCCCC (18)
$\nu38$	A′		207	306	301	331, 324	325, 318	δC−COOH (55) + δCCCl (37)
$\nu39$	A′		174	177	174	219, 202	215, 199	δC−COOH (50) + δCCCl (38)
$\nu40$	A″		142	145	142	164, 152	161, 149	τCCCC (45) + τCCCO (22) + τCCCCl (15)
$\nu41$	A″			135	132	133, 132	131, 130	τCCCO (40) + τCCCCl (24) + τCCCC (21)
$\nu42$	A″		85	81	80	88, 75	87, 74	tCOOH (78)
σ (rms)				87.977	36.112			
R^2				0.9987	0.9991			

ν; stretching, δ; in-plane bending, γ; out-of-plane bending, τ; torsion, t; twisting.

distribution. The symmetry species of all the vibrations are given in the second column of the Tables 3 and 4. Modes are numbered from biggest to smallest wavenumber within each fundamental wavenumbers, ν. All vibrations are active in both IR absorption and Raman scattering.

Figures 3 and 4 present the experimental and calculated infrared and Raman spectra. The calculated IR and Raman spectra are shown in figures for comparative purposes, where the calculated intensity is plotted against the harmonic vibrational wavenumbers. The experimental wavenumbers are tabulated in Tables 3 and 4 together with the calculated wavenumbers for the monomer and dimer C1 conformer of studied molecules individually. The

resulting vibrational wavenumbers for the optimized geometries and the proposed vibrational assignments are given in the tables. The last column gives a detailed description of the normal modes based on the TED.

Owing to lack of enough detailed experimental data for these molecules, the vibrational spectra were obtained by molecular orbital calculation using the Gaussian03[31] program. Vibrational modes of the molecules were researched by harmonic wavenumbers calculations performed at the corresponding energy optimized geometries. The assignment of the vibrational absorptions was made by the comparison with the related molecules and also with the results obtained from the theoretical
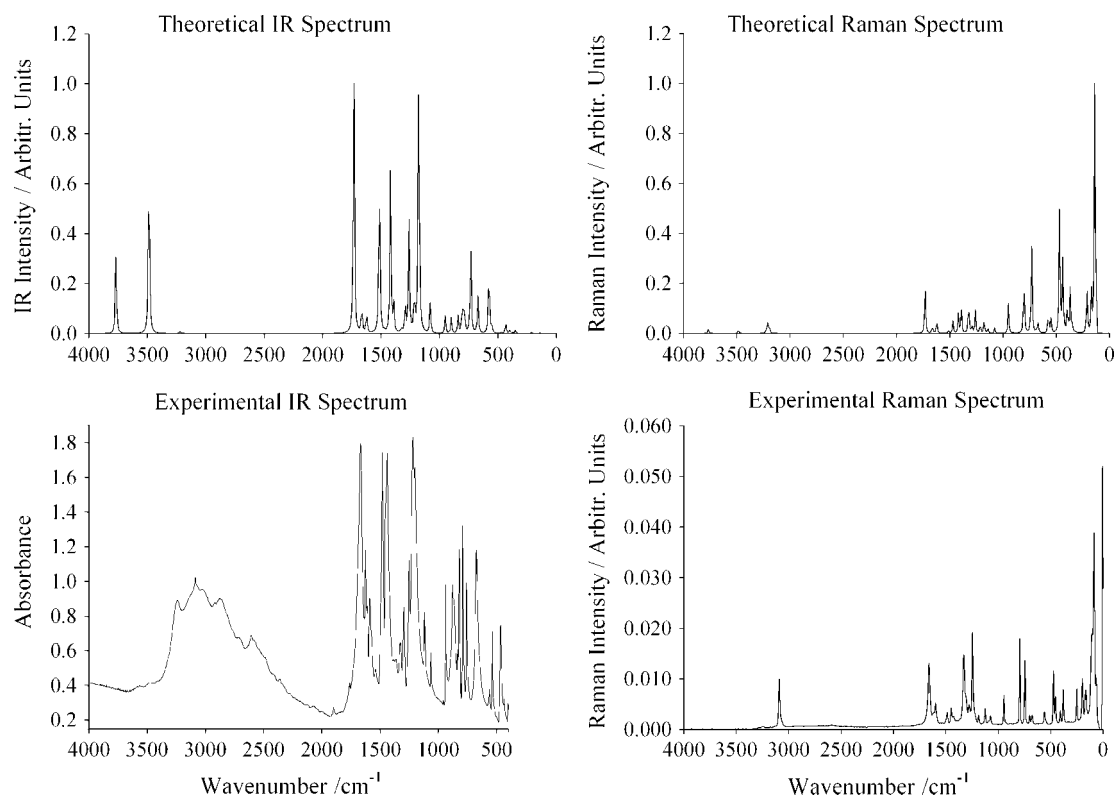

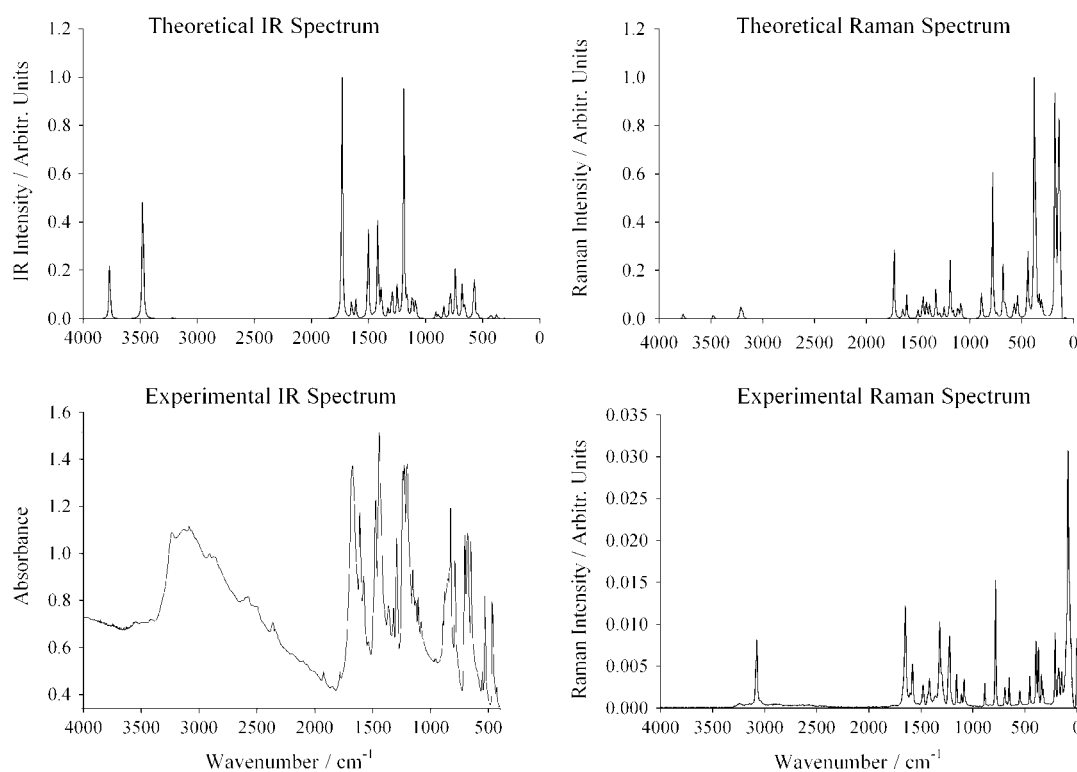**Figure 3.** Calculated and experimental infrared and Raman spectrum of 5-FSA molecule.

Figure 4. Calculated and experimental infrared and Raman spectrum of 5-ClSA molecule.

calculations. As seen in Tables 3 and 4, there is great mixing of the ring vibrational modes and also between the ring and substituent modes. The descriptions of the modes are very complex because of the low symmetry of the studied molecules. Especially, in-plane modes and out-of-plane modes are the most difficult to assign due to mixing with the ring modes and also with the substituent modes. But there are some strong wavenumbers useful to characterize in the IR and Raman spectra.

It is worth mentioning that, however, in solid 5-FSA and 5-ClSA, the COOH group and the ring OH group are involved in inter- and intrahydrogen bonding interactions. In the crystal lattice, dimeric molecules, held together by hydrogen bridges between carboxyl groups, are arranged.[27,28] In order to simulate the H-bonding through the COOH group, we also calculate vibrational wavenumbers of 5-FSA and 5-ClSA dimer of C1 conformers (Tables 3 and 4).

Between 1350 and 400 cm^{-1}, several characteristic in-plane deformations C–H, out-of-plane C–H vibrations as well as out-of-plane (CCC) deformations are observed. Two of the mixed modes involving contributions from CC stretching as well as OH in-plane deformations are observed in the range 1500–1350 cm^{-1}. In the range of 1800–1500 cm^{-1}, the CC, C=O and COOH group stretching vibrations occur. In the spectral range over 3000 cm^{-1}, O–H and C–H stretching modes take place.[41]

The O–H vibrations are extremely sensitive to formation of hydrogen bonding. The O–H stretching band is characterized by a very broad band appearing near about 3400–3600 cm^{-1}. Additionally, a group of atoms experiencing a change in its environment generally shows a shift in its IR absorption. For salicylic acid, the O–H vibration is observed to 3238 cm^{-1} in FT-IR spectra.[10] Krishnakumar and Mathammal[42] observed the O–H stretching vibration at 3500 cm^{-1} for 3,5-dichloro salicylic acid. This band for 5-BrSA is observed at 3551 and 3250 cm^{-1}

and also calculated at 3610 and 3334 cm^{-1}.[16] For our title molecules, these bands calculated at 3609 and 3339 cm^{-1} (5-FSA) and 3608 and 3330 cm^{-1} (5-ClSA) which modes are (ν1, ν2) of O$_{11}$–H$_{12}$, O$_{14}$–H$_{15}$ units, respectively. They are intramolecular and intermolecular hydrogen bonds, respectively. These modes are almost 100% stretching modes as it is evident from the TED column. These wavenumbers are observed at 3546 and 3233 cm^{-1} for 5-ClSA, but only ν2 wavenumber is observed at 3244 cm^{-1} FT-IR experimentally for 5-FSA. As discussed in our previous papers,[16,43,44] with the halogen (F, Cl, Br, . . .) substitution, O–H stretching vibrations shifted to higher wavenumbers region.[45] This means that, the O–H vibrations are sensitive due to halogen coordination. For 3-, 4-, 5-amino-salicylic acid,[3] this vibration is observed at 3338, 3397 and 3409 cm^{-1}, respectively. The O–H in-plane bending vibration appears in the range of 1440–1395 cm^{-1}.[46,47] Krishnakumar and Mathammal[42] observed the in-plane bending vibration at 1463 cm^{-1} in the FT-IR for 3,5-dichloro salicylic acid. This vibration is observed at 1461, 1450 and 1454 cm^{-1} for 3-, 4-, 5-amino-salicylic acid.[3] Akkaya and Akyüz[25] assigned this vibration at 1294 and 1160 cm^{-1} in the IR for 4-amino-salicylic acid. For 3-amino-salicylic acid, this band is observed at 1340 cm^{-1} and 1171 cm^{-1} which is a motion of hydroxyl group.[26] In our previous paper on 5-BrSA,[16] the O–H in-plane bending is assigned to 1441 cm^{-1} in FT-IR and 1411 cm^{-1} in FT-Raman, which are calculated at 1425 and 1392 cm^{-1}. In the present work, the O–H in-plane bending mode is assigned to 1443 cm^{-1} and 1385 cm^{-1} in FT-IR and 1446 cm^{-1} in FT-Raman experimentally, which are calculated at 1446 and 1395 cm^{-1} for 5-FSA. For 5-ClSA, the O–H in-plane bending mode is observed at 1443 cm^{-1} in FT-IR and 1430 and 1413 cm^{-1} in FT-Raman which are calculated at 1429 and 1393 cm^{-1}. The O–H out-of-plane bending modes ν25 (O11–H12) and ν26 (O14–H15) of 5-FSA are observed at 761 cm^{-1} in the FT-IR and 744 cm^{-1} in the FT-Raman. For 5-ClSA,

the O–H out-of-plane bending modes $\nu26$ (O14–H15) and $\nu30$ (O11–H12) are assigned to 704 cm^{-1} and 554 cm^{-1} in the FT-IR. The O–H out-of-plane bending mode is observed at 625 cm^{-1} by Akkaya and Akyüz[25] for 4-amino-salicylic acid. The O–H in-plane bending and out-of-plane bending vibrations values in dimer conformations are increasing, because of the hydrogen-bonding effect through the carboxyl groups (Tables 3 and 4).

The heteroaromatic structure shows the presence of the C–H stretching vibrations in the 3000–3100 cm^{-1} range which is the characteristic region for the ready identification of C–H stretching vibrations.[47] This means that, the three adjacent hydrogen atoms left around the benzene ring, the 5-FSA and 5-ClSA give rise to three C–H stretching modes ($\nu3$–$\nu5$), three C–H in-plane bending ($\nu13$, $\nu15$, $\nu18$) and ($\nu13$, $\nu15$, $\nu17$) and three C–H out-of-plane bending ($\nu20$, $\nu22$, $\nu23$) and ($\nu20$, $\nu21$, $\nu23$) for 5-FSA and 5-ClSA vibrations. The vibrations assigned to aromatic C–H stretching in the range 3066–3144 cm^{-1}[16,47,48] are in agreement with experimental assignment at 3090 cm^{-1} and 3074 cm^{-1} FT-IR (3087 cm^{-1} FT-Raman). In previous work[16] (5-BrSA), these modes are calculated from 3086 to 3058 cm^{-1} which is in good agreement with the experimental values at 3061 cm^{-1} FT-IR and 3075 cm^{-1} FT-Raman for the most stable conformer. In this work, the C–H stretching modes of 5-FSA are calculated in the range of from 3088 to 3059 cm^{-1} and these values are calculated in the range of 3086–3059 cm^{-1} for 5-ClSA for the most stable C1 conformers. They are very pure modes since their TED contribution are 100%. The $\nu4$ and $\nu5$ modes are symmetric and antisymmetric stretching vibrations, respectively. In aromatic compounds, the C–H in-plane bending wavenumbers appear in the range of 1000–1300 cm^{-1} and the C–H out-of-plane bending vibration in the range 750–1000 cm^{-1}.[47–49] In 5-BrSA, the C–H in-plane bending modes occur to the FT-IR and FT-Raman bands at 1312, 1222 and 1318, 1226, 1152 cm^{-1}, respectively.[16] Therefore, the C–H in-plane bends of 5-FSA are assigned to the FT-IR and FT-Raman bands at 1299, 1222, 1122 and 1326, 1245, 1122 cm^{-1}, respectively. The calculated values of the C–H in-plane bends of 5-FSA are 1302, 1240 and 1123 cm^{-1}, which shows good agreement with the experimental values. For 5-ClSA, these vibrations are observed at 1318, 1228, 1129 and 1316, 1224, 1154 cm^{-1} in FT-IR and FT-Raman, respectively. Also the C–H in-plane bends of 5-ClSA are calculated as 1305, 1227 and 1143 cm^{-1}, which shows good agreement with the experimental values. The C–H out-of-plane bends are assigned to the FT-IR bands in the range from 954 to 826 cm^{-1} are not observed in the Raman spectrum. These bands are calculated from 957 to 826 cm^{-1} which are in good agreement with experimental values. For 5-FSA, these are assigned to the FT-IR bands in the range from 958 to 822 cm^{-1} and are observed at 942 cm^{-1} in the Raman spectrum. The change in the wavenumbers of these deformations from the values in benzene is almost determined exclusively by the relative position of the substituents and is almost independent of their nature.[50] Both the in-plane and out-of-plane bending vibrations are illustrated as mixed modes. The TED contributions of the in-plane and out-of-plane modes indicate that out-of-plane modes are also highly pure modes like the in-plane bending fundamentals. The C–H in-plane and C–H out-of-plane of 4-amino-salicylic acid were assigned to 1369, 1228, 1108 cm^{-1} and from 819 to 970 cm^{-1}, respectively, by Akkaya and Akyüz.[25] These bands are observed at 1229, 1150, 1068 cm^{-1} and 962, 781 cm^{-1} in-plane and out-of-plane, respectively, for 3-amino-salicylic acid.[26]

Derivatives of carboxylic acids are characterized by several intense absorptions in the infrared spectrum. The most characteristic feature of carboxylic group is a single band observed usually in the 1700–1800 cm^{-1} region. This band is due to the C=O stretching vibration. In the solid state, most of carboxylic acids form a dimeric structure that is due to the result of hydrogen bonding between two neighboring –COOH groups. In such a case, two ν(C=O) are expected: one that is Raman active (in-phase, symmetric stretching vibration) and the other one, out-of-phase (antisymmetric stretching vibration), is IR active only. The asymmetric stretch is usually at higher wavenumber than the symmetric stretch. Therefore, the C=O stretching mode ($\nu6$, asymmetric stretching vibration) is observed at 1670 cm^{-1} in FT-IR spectrum and observed at 1660 cm^{-1} (symmetric stretching vibration) in FT-Raman spectrum for 5-FSA. This mode of 5-ClSA ($\nu6$, asymmetric stretching vibration) is observed at 1675 cm^{-1} in FT-IR spectrum and observed at 1648 cm^{-1} (symmetric stretching vibration) in FT-Raman spectrum. The theoretical value of C=O band is computed at 1660 cm^{-1}, which is in very good agreement with experimental results. We observed this band at 1660 cm^{-1} (asymmetric stretching vibration) in FT-IR spectrum and observed at 1629 cm^{-1} (symmetric stretching vibration) in the FT-Raman spectrum for 5-BrSA.[16] Because of the hydrogen-bonding effect the carboxyl groups, the C=O stretching model of C1 dimer conformation was calculated for 5-FSA and 5-ClSA at 1668, 1652 cm^{-1} and 1665, 1664 cm^{-1} respectively. By the substitutions in place of hydrogen atom, the substitutions position *versus* carboxylic anion influence the C=O mode form remarkably. For salicylic acid, the C=O stretching mode is observed at 1662 cm^{-1} in the FT-IR spectrum.[10] The C=O stretching mode is assigned at 1538, 1592 and 1584 cm^{-1} for 3-, 4- and 5-amino-salicylic acid, respectively.[2] In 4-amino-salicylic acid, the C=O stretching mode is observed at 1659 cm^{-1} with the strongest absorption in the IR spectrum which is predicted at 1642 cm^{-1} by Akkaya and Akyüz[25] Nogueira[26] observed this band at 1649 and 1652 cm^{-1} IR and Raman spectra for 3-amino-salicylic acid.

Empirical assignments of vibrational modes for peaks in the fingerprint region are difficult. In the wavenumber region of 600–1660 cm^{-1}, the spectrum observed in the experiments closely resembles the calculated spectrum, except for differences in details. These wavenumbers in the same range are in reasonable agreement with experimental results (Tables 3 and 4) for each molecule. The ring stretching vibrations are very much important in the spectrum of benzene and its derivatives are highly characteristic of the aromatic ring itself. The ring carbon–carbon stretching vibrations appear in the region 1400–1650 cm^{-1} in benzene derivates.[47–49,51] In general, the bands of variable intensity are observed at 1625–1590, 1590–1575, 1540–1470, 1465–1430 and 1380–1280 cm^{-1} from the wavenumber ranges by Varsanyi.[49] For 3-amino-salicylic acid, the CC stretching modes are observed in the range from 1460 to 1567 cm^{-1} in IR and from 1456 to 1572 cm^{-1} in Raman spectra.[26] Akkaya and Akyüz[25] assigned 1642 cm^{-1} IR band for 4-amino-salicylic acid. The highest CC stretching modes in 5-BrSA[16] is observed at 1606 cm^{-1} in the FT-IR spectrum. As revealed by TED, the ring CC stretching modes are observed at 1628, 1591, 1443, 1329, 1254 cm^{-1} for 5-FSA and 1610, 1576, 1443, 1361, 1292 cm^{-1} for 5-ClSA. The ring-breathing mode which can be described as the 'trigonal ring breathing' vibration or the 'star of David' vibration[52,53] of the aromatic ring at ($\nu18$) 1096 cm^{-1} for 5-ClSA, which is observed at 1106 cm^{-1} in the FT-IR and FT-Raman spectra, however, in 5-FSA is observed at 794 cm^{-1} ($\nu24$) in the both spectra. The theoretically computed value shows very good agreement with experimental results (Tables 3 and 4). For 4-amino-salicylic acid, the ring-breathing mode is predicted at 960–969 cm^{-1} for the

most stable conformers which is observed at 955 cm^{-1} in the IR and at 962 cm^{-1} in the Raman spectra.[25] The theoretically calculated C–C–C in-plane and out-of-plane bending modes have been obtained to be consistent with the recorded spectral values. The ring assignments proposed in this study is also in agreement with literature values.[25,26,43,46]

Mooney[54] assigned vibrations of the C–X group (X = F, Cl, Br, I) in the wavenumber range of 1129–480 cm^{-1}. In benzene derivatives containing a Cl group, the C–Cl stretching wavenumber occurs in the region 600–800 cm^{-1}.[48,55] However, vibrational coupling with other vibrations may shift the upper limit to 840 cm^{-1}.[48] The assignments of the C–F and C–Cl stretching and deformation vibrations have been made on the basis of the calculated TED. Involving the ring-halogen modes are related partially to C–X (X: F, Cl, Br, . . .) stretching and bending modes. The theoretical wavenumbers of C–X stretching vibration coupled with other group vibrations. Some vibrational modes were shown to be X-sensitive modes, whereas others were calculated in a narrow wavenumber range. In view of this, the band in FT-IR at 651 cm^{-1} having a very strong Raman counterpart at 649 cm^{-1} is assigned to the C–Cl stretching of 5-ClSA. Krishnakumar and Mathammal[42] observed in Raman spectrum at 850 and 749 cm^{-1} was assigned to the C–Cl stretching mode of 3,5-dichloro salicylic acid. The wavenumber 631 cm^{-1} is observed with strong infrared and Raman intensities is assigned to C–Cl stretching mode by Shanker et al.[56] According to the calculated TED, our calculations show that there is no pure C–X band vibration. An intense calculated infrared band at 645 cm^{-1} (ν29) in 5-ClSA can be assigned to the C–Cl stretching vibration. This mode is extensively mixed with other modes. The C–Cl band is assigned at 651 cm^{-1} in FT-IR (649 cm^{-1} in FT-Raman). However, in the present case, the TEDs for calculated wavenumbers at 374 cm^{-1} and 360 cm^{-1} also appear in the C–Cl stretching mode (ν35, ν36). The C–Cl in-plane bending modes have strong to medium intensity generally in the region 450–250 cm^{-1}. Krishnakumar and Mathammal[42] observed that the strong band at 315 cm^{-1} was assigned to the C–Cl in-plane bending and the band observed at 335 and 130 cm^{-1} was assigned to the C–Cl out-of-plane bending mode of 3,5-dichloro salicylic acid. In this study, two low-energy modes are generated by the chlorination of the salicylic acid ring, at 301 and 174 cm^{-1}, in-plane δ(C–Cl), and 326 and 132 cm^{-1}, out-of-plane τ(C–Cl), for 5-ClSA. This is in agreement with the literature.[42,49,54]

An assignment of the C–F stretching modes is very difficult as these modes are strongly coupled with the other in-plane modes. Normally, the intensity of the C–F stretching vibrations is very strong in the IR spectra and these appear in the range 1000–1300 cm^{-1} as assigned earlier.[57,58] Infrared spectra of substituted fluorine derivatives have assigned the wavenumber 1250 cm^{-1} to C-F stretching mode of vibration which have been studied by Narasimham et al.[59] The C–F stretching is observed in the region 1250–1350 cm^{-1}.[60,61] Based on the above literature value, we have assigned the strong bands at 1254 and 1222 cm^{-1} in the FT-IR spectrum due to the C-F stretching mode. Their counterpart in the Raman spectrum is at 1274 and 1245 cm^{-1}. The theoretically computed scaled value of 1271 and 1240 cm^{-1} (modes no. 14 and 15) at B3LYP/6-311+G(d, p) shows good agreement with experimental results. The C-F in-plane bending and out-of-plane bending wavenumbers are assigned at 402 cm^{-1} and 377 cm^{-1} in FT-Raman, respectively. The remainder of the observed and calculated wavenumbers is accounted in Tables 3 and 4.

The correlation coefficients and root mean square (RMS) (σ) values based on these calculations are presented in the bottom of Tables 3 and 4 to make comparison with experimental values of infrared wavenumbers, and correlation coefficients (R^2) were found at 0.9994 and 0.9991 for 5-FSA and 5-ClSA molecules, respectively. The RMS errors of the wavenumbers between the unscaled and experimentally observed were found to be 64.637 and 87.977, whereas after scaling it was found to be 21.989 and 36.112 for C1 conformation of 5-FSA and 5-ClSA molecules, respectively. When we summarize, the experimental fundamentals are in better agreement with the scaled fundamentals and are found to have a good correlation for DFT/B3LYP method.

Bond distances and characteristic wavenumbers

The molecular structure of a most stable conformation has been widely investigated not only by experimental methods but also by theoretical approaches. Salicylic acid and its derivatives establish one of the most popular model systems for studying inter- and intramolecular hydrogen bonds. In order to compare the strength of inter- and intramolecular hydrogen bonding, some pieces of evidence from geometrical and vibrational motion behavior were chosen to identify the hydrogen-bonding effect. Table 5 shows the bond distances and the characteristic wavenumbers of atoms within various conformers or isomers. The relationships between these distances and the strengths of hydrogen bonds are discussed here. Based on these calculated values, we conclude the following.

(1) Among the eight conformers of 5-FSA and 5-ClSA, the C1 has the longest carbonyl distance ($d_{C=O}$ = 1.225 Å), longer than others, and it has the smallest wavenumber ($\nu_{C=O}$) 1660 cm^{-1}.
(2) Due to the O atom in O=COH of the C1 and C3 conformer, which donates electron to form with H in hydroxyl only, they have the longest hydroxyl distances ($d_{O14-H15}$) (0.981 and 0.985 Å for 5-FSA, 0.981 and 0.986 Å for 5-ClSA, respectively) and the smallest wavenumbers (ν_{O-H}) 3339 and 3263 cm^{-1} for 5-FSA and 3330 and 3253 cm^{-1} for 5-ClSA.
(3) As affected by intra-hydrogen bonding, conformers have longer OH distances (d_{O-H}) and smaller wavenumbers ν_{O-H} than other conformers/isomers.
(4) The calculated wavenumbers for dimer (intermolecular hydrogen bonding) 5-FSA and 5-ClSA shown in Fig. 2 are tabulated in Tables 3 and 4. As seen in these tables, the inter-hydrogen bonding effect through the carboxyl groups is clearly observed (e.g. in ν1, ν2, ν6, ν11, ν14, ν17, and ν30 modes).

These results are in agreement with literatures.[16,23,25,44]

Conclusions

In this study, we have performed the experimental and theoretical vibrational analysis of 5-FSA and 5-ClSA, for the first time. A comparison of the result of experimental and theoretical study gave us a full description of the geometry and vibrational properties of these molecules. The comparison between hydrogen bond distances and bond energy indicates the C1 conformer is found to be the most stable conformer for each molecule. Intermolecular and intramolecular hydrogen bonding between H and O is expected in C1 conformer. Dimeric molecules held together by hydrogen bridges between carboxyl groups. The calculated distances ($d_{C=O}$,

Table 5. The bond distances (Å) and characteristic wavenumbers (cm^{-1}) related to C=O bond and O–H bonds

	C=O bond	Scaled wavenumbers	O–H bond	Scaled wavenumbers	O–H bond	Scaled wavenumbers
	$D_{C10=O13}$	$\nu_{C10=O13}$	$D_{O11–H12}$	$\nu_{O11–H12}$	$D_{O14–H15}$	$\nu_{O14–H15}$
5-FSA form						
C1	1.225	1660	0.969	3610	0.981	3340
C2	1.205	1722	0.969	3610	0.970	3543
C3	1.219	1677	0.964	3668	0.985	3263
C4	1.204	1730	0.972	3515	0.963	3681
C5	1.211	1693	0.969	3599	0.963	3666
C6	1.205	1723	0.968	3619	0.964	3661
C7	1.198	1745	0.962	3686	0.964	3658
C8	1.200	1728	0.958	3738	0.956	3761
5-ClSA frorm						
C1	1.225	1660	0.969	3610	0.982	3330
C2	1.205	1722	0.969	3610	0.970	3536
C3	1.219	1678	0.964	3667	0.986	3253
C4	1.204	1730	0.971	3519	0.963	3678
C5	1.211	1694	0.969	3599	0.964	3663
C6	1.205	1722	0.968	3619	0.964	3659
C7	1.199	1745	0.962	3684	0.964	3655
C8	1.200	1729	0.956	3737	0.956	3759

$d_{O–H}$) and the characteristic wavenumbers ($\nu_{C=O}$, $\nu_{O–H}$) show that when an inter- and intra-hydrogen bonding between C=O and H–O exists, the distances within C=O and within O–H get longer and the characteristic wavenumbers ($\nu_{C=O}$, $\nu_{O–H}$) become smaller. The calculated geometric parameters and vibrational wavenumbers obtained with density functional theory calculations (B3LYP/6-311++G(d,p)) method are in well agreement with the experimental values obtained for the investigated molecules.

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