

## FTIR, FT-Raman and Quantum Chemical calculations of 3,5-dichlorosalicylic acid

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### Abstract

IR and Raman spectra of 3,5-dichlorosalicylic acid were recorded and analyzed. Using Gaussian03 set of quantum chemistry codes, the vibrational wavenumbers and corresponding vibrational assignments were examined theoretically. The results indicate that the SDD method is able to provide satisfactory results for predicting the vibrational wavenumbers. The predicted infrared intensities and Raman activities are reported.

*Key words:* DFT calculations, salicylic acid, IR, Raman

### Introduction

Salicylates in their derivatized forms are widely used in medicine<sup>1</sup>. In addition to analgesic, antipyretic and anti-inflammatory properties, salicylates possess also some other actions that have been proved to be therapeutically beneficial<sup>2,3</sup>. Unfortunately, a number of side effects are associated with the use of salicylates, most notable being gastrointestinal disturbances such as dyspepsia, gastroduodenal bleeding, gastric ulcerations and gastritis<sup>4,5</sup>. Vibrational spectroscopic studies and SERS spectra have been reported for salicylic acid<sup>6</sup>, 3-aminosalicylic acid<sup>7</sup>, sodium salicylate<sup>8</sup>, 4-aminosalicylic acid

sodium salt dihydrate<sup>9</sup>, methyl salicylate<sup>10</sup>, 5-sulphosalicylic acid<sup>11</sup> and ethyl salicylate<sup>12</sup>. In the present work, the FT-IR and FT-Raman spectra of 3,5-dichlorosalicylic acid were recorded and analyzed. The vibrational wavenumbers were compared with theoretically calculated wavenumbers.

### Experimental

The FT-IR spectrum was recorded using a Bruker IFS 28 spectrometer with KBr pellets, number of scans 16, resolution 2 cm<sup>-1</sup>. The FT-Raman spectrum was obtained on a Bruker Equinox 55/s spectrometer with FRA Raman socket, 106/s. For excitation of the

spectrum the emission of Nd:YAG laser was used, excitation wavelength 1064 nm, laser power 250 mW, resolution  $2\text{ cm}^{-1}$ .

#### *Computational details :*

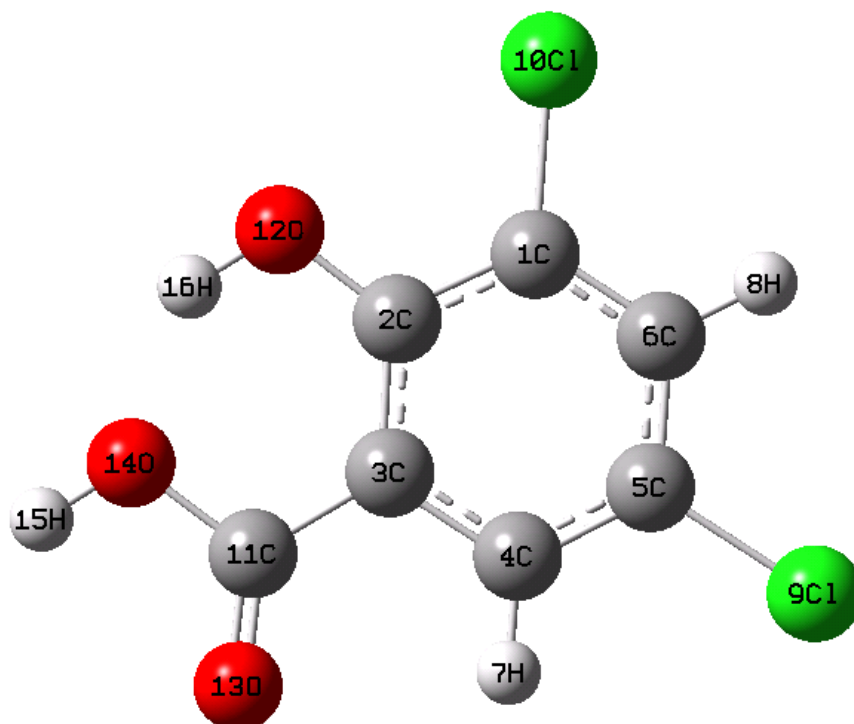
Calculations of the title compound were carried out with Gaussian03 software program<sup>13</sup> using the B3LYP/6-31G\* and B3LYP/SDD basis sets to predict the molecular structure and vibrational wavenumbers. Calculations were carried out with Becke's three parameter hybrid model using the Lee-Yang-Parr correlation functional (B3LYP) method. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence to minima on the potential surface. At the optimized structure of the examined species, no imaginary wavenumber modes were obtained, proving that a true minimum on the potential surface was found. The DFT hybrid B3LYP functional tends also to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data. Therefore, a scaling factor of 0.9613 was uniformly applied to the DFT calculated wavenumbers<sup>14</sup>. The observed disagreement between theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry.

#### **Results and Discussion**

The observed IR, Raman bands and

calculated (scaled) wavenumbers and assignments are given in table 1.

The  $-\text{C}(=\text{O})\text{OH}$  group is best characterized by the OH stretch, the  $\text{C}=\text{O}$  stretch and the OH out-of-plane deformation as well as the C-O stretch and the OH in-plane deformation. In the present case the DFT calculations give the OH stretch at  $3533\text{ cm}^{-1}$ . The  $\text{C}=\text{O}$  stretching vibration gives rise to characteristic bands in the IR and Raman spectra and the intensity of these bands can increase due to conjugation or the formation of hydrogen bonds<sup>15</sup>.  $\text{C}=\text{O}$  stretching<sup>16</sup> vibration gives rise to a strong band in the region  $1725\pm65\text{ cm}^{-1}$ . Rippon *et al.*<sup>17</sup> reported a value of  $1647\text{ cm}^{-1}$  for the carbonyl stretching mode. The band observed at  $1668\text{ cm}^{-1}$  in the IR spectrum,  $1695$  in the Raman spectrum and at  $1648\text{ cm}^{-1}$  (SDD) is assigned as  $\nu\text{C}=\text{O}$  mode. The OH in-plane deformation, coupled to the C-O stretching vibration is expected in the region  $1390\pm55\text{ cm}^{-1}$ . The  $\text{C}(=\text{O})\text{O}$  stretching vibration, coupled to the OH in-plane deformation, exhibits a moderate to strong band in the region  $1250\pm80\text{ cm}^{-1}$ . The DFT calculations give OH in-plane deformation at  $1445$  and C-O stretch at  $1248\text{ cm}^{-1}$ . The out-of-plane deformation<sup>18</sup>  $\gamma\text{OH}$  exhibits a moderate band in the region  $905\pm65\text{ cm}^{-1}$ . The  $\text{C}=\text{O}$  in-plane deformation is weakly to moderately active in the region  $725\pm95\text{ cm}^{-1}$ . Most carboxylic acid display  $\gamma\text{C}=\text{O}$  in the region  $595\pm85\text{ cm}^{-1}$  in the vicinity of methyl and ethyl esters. The  $-\text{C}(=\text{O})\text{O}$  deformation or rock has a weak to moderate intensity and appears in the region  $445\pm125\text{ cm}^{-1}$ . The  $\text{C}=\text{O}$  deformation bands are identified assigned (Table 1).



The SDD calculations give the OH stretching bands at  $3327\text{ cm}^{-1}$ . The in-plane deformation<sup>16</sup> is expected in the region  $1400\pm 40\text{ cm}^{-1}$  and the band at  $1359\text{ cm}^{-1}$  in the IR spectrum is assigned as the in-plane deformation of OH band. The calculated value is  $1350\text{ cm}^{-1}$ . The stretching mode of the hydroxyl group with respect to the phenyl moiety C-O appears at  $1229\text{ cm}^{-1}$  in the IR spectrum,  $1232\text{ cm}^{-1}$  in the Raman spectrum and the calculated value are  $1223\text{ cm}^{-1}$ . This band is expected in the region<sup>19,20</sup>  $1220\pm 40\text{ cm}^{-1}$ . El-Shahway *et al.*<sup>21</sup> reported C-O stretching at  $1240\text{ cm}^{-1}$ .

The aromatic CH stretching vibrations<sup>16</sup> absorb weakly to moderately between  $3120\text{--}3000\text{ cm}^{-1}$ . The SDD calculations give bands

at  $3122, 3124\text{ cm}^{-1}$ . Experimentally we have observed bands at  $3095, 3074\text{ cm}^{-1}$  in the IR spectrum and at  $3096, 3076\text{ cm}^{-1}$  in the Raman spectrum. The benzene ring possesses six ring stretching vibrations of which the four with the highest wavenumbers occurring near  $1600, 1580, 1490$  and  $1440\text{ cm}^{-1}$  are good group vibrations<sup>16</sup>. With heavy substituents, the bands tend to shift to somewhat lower wavenumbers and the greater the number of substituents on the ring, the broader the absorption regions<sup>16</sup>. In the case of C=O substitution, the band near  $1490\text{ cm}^{-1}$  can be very weak<sup>16</sup>. The fifth ring stretching vibration is active near  $1315\pm 65\text{ cm}^{-1}$  a region that overlaps strongly with that of the CH in-plane deformation<sup>16</sup>. The sixth ring stretching vibration, the ring breathing

Table 1. Observed IR, Raman bands, Scaled wavenumbers and assignments

B3LYP/6-31G*			B3LYP/SDD			IR $\nu$ ( $\text{cm}^{-1}$ )	Raman $\nu(\text{cm}^{-1})$	Assign ments
$\nu$ ( $\text{cm}^{-1}$ )	IR <sub>I</sub>	R <sub>A</sub>	$\nu$ ( $\text{cm}^{-1}$ )	IR <sub>I</sub>	R <sub>A</sub>			
3500	85.64	209.70	3533	101.92	180.06	3416		$\nu\text{OH}$
3312	316.11	99.53	3327	327.61	98.10	3406		$\nu\text{OH}$
3132	0.81	75.37	3124	1.06	70.91	3095	3096	$\nu\text{CH}$
3131	6.01	31.72	3122	4.85	28.58	3074	3076	$\nu\text{CH}$
1677	314.14	73.71	1648	379.96	98.87	1668	1695	$\nu\text{C=O}$
1607	67.60	42.74	1594	71.30	55.48	1604	1588	$\nu\text{Ph}$
1547	6.04	10.63	1538	4.57	15.03			$\nu\text{Ph}$
1466	106.19	5.74	1445	112.68	7.18	1449	1433	$\delta\text{OH}$
1412	102.02	1.82	1394	100.30	1.99		1383	$\nu\text{Ph}$
1360	69.35	3.14	1350	41.65	4.01	1359		$\delta\text{OH}$
1306	93.60	29.81	1292	135.83	35.01	1299	1308	$\nu\text{Ph}$
1271	141.58	6.38	1248	113.15	7.69	1267	1269	$\nu\text{CO}$
1244	144.57	4.65	1223	169.30	4.55	1229	1232	$\nu\text{CO}$
1201	125.72	14.35	1186	130.21	12.33	1186	1177	$\delta\text{CH}$
1128	101.07	11.40	1114	94.22	13.03	1098	1100	$\nu\text{Ph}$
1089	11.94	6.42	1074	14.68	7.96			$\delta\text{CH}$
1033	148.76	20.44	1007	143.02	23.02			$\nu\text{Ph}$
938	6.75	0.88	929	9.03	1.09		923	$\gamma\text{CH}$
909	19.56	0.34	894	19.37	1.39	894	892	$\gamma\text{CH}$
850	22.03	14.06	834	24.08	14.57	835	850	$\nu\text{CC}$
797	17.32	7.18	784	16.52	7.67	793	790	$\gamma\text{OH}$
768	32.88	0.30	766	38.31	0.40	762	749	$\delta\text{C=O}$
714	131.23	1.02	719	171.94	1.85	707		$\gamma\text{OH}$
698	92.27	6.38	687	86.31	7.30		697	$\nu\text{CCl}$
672	84.07	1.18	673	48.82	0.19	650		$\nu\text{CCl}$
617	42.19	3.33	603	30.10	4.77	609		$\gamma\text{C=O}$
595	38.32	1.50	581	45.65	1.90			$\delta\text{Ph}$
580	157.31	6.64	567	155.88	3.62	562		$\gamma\text{Ph}$
563	0.11	0.81	551	1.57	2.31			$\rho\text{C(=O)O}$
462	4.62	4.09	454	3.64	3.32	478	467	$\delta\text{Ph(X)}$
415	6.77	4.18	408	6.51	4.90		418	$\gamma\text{Ph(X)}$
405	4.99	0.72	395	4.22	0.82			$\delta\text{Ph(X)}$
362	0.95	3.55	355	1.33	3.92		360	$\delta\text{CCl}$

345	0.95	0.07	338	0.94	13.95	336	$\delta\text{CCl}$
343	1.11	12.04	336	1.72	0.01		$\gamma\text{Ph(X)}$
316	2.79	7.34	309	3.23	8.35		$\gamma\text{Ph(X)}$
197	0.13	1.58	192	0.06	1.33	204	$\gamma\text{CCl}$
177	0.78	2.65	174	0.73	2.84	170	$\gamma\text{CCl}$
164	0.04	2.97	161	0.07	3.06	168	tCCl
134	1.08	0.17	131	0.67	0.11		tCOH
102	1.46	0.05	99	2.28	0.03		tCOOH
70	2.00	0.44	69	2.44	0.41		tPh

$\nu$ -stretching;  $\delta$ -in-plane deformation;  $\gamma$ -out-of-plane deformation; t-torsion; Ph-phenyl ring; IR<sub>I</sub>-IR intensity; R<sub>A</sub>-Raman activity; X-substituent sensitive.

mode appears as a weak band near 1000 cm<sup>-1</sup> in mono, 1,3-di, and 1,3,5-trisubstituted benzenes. In the otherwise substituted benzenes, however, this vibration is substituent sensitive and difficult to distinguish from the other modes. The benzene ring stretching vibrations  $\nu\text{Ph}$  are expected in the region<sup>16</sup> 1620- 1200 cm<sup>-1</sup> and in the present study the bands observed at 1604, 1299, 1098, in the IR spectrum, 1588, 1383, 1308, 1100, in the Raman spectrum and 1594, 1538, 1394, 1292, 1114, 1007 cm<sup>-1</sup> (SDD) are assigned as benzene ring stretching vibrations. The CH in-plane and out-of-plane deformation bands of the phenyl ring are expected above and below 1000 cm<sup>-1</sup>, respectively<sup>16</sup>. These bands are also identified and assigned (Table 1).

The aliphatic CCl bonds absorb<sup>20</sup> at 830-560 cm<sup>-1</sup> and putting more than one chlorine on a carbon atom raises the CCl wavenumber. The CCl<sub>2</sub> stretching mode is reported at around 738 cm<sup>-1</sup> for dichloromethane and scissoring mode<sup>19,20</sup>  $\delta\text{CCl}_2$  around 284 cm<sup>-1</sup>. For 2-cyanophenylisocyanide dichloride the  $\nu\text{CCl}$  stretching mode is reported

at 870 cm<sup>-1</sup> (IR), 877 (Raman) and at 882 cm<sup>-1</sup> theoretically<sup>22</sup>. Arslan *et al.*<sup>23</sup> reported  $\nu\text{CCl}$  at 683 cm<sup>-1</sup> (experimentally) and at 711, 736, 687, 697 cm<sup>-1</sup> theoretically. The deformation bands of CCl are reported<sup>23</sup> at 431, 435, 441 and 443 cm<sup>-1</sup>. In the present case the bands at 687, 673 (SDD), 650 (IR) and 697 cm<sup>-1</sup> (Raman) are assigned as  $\nu\text{CCl}$  bands. The deformation bands of the CCl are assigned below 400 cm<sup>-1</sup>.

## Conclusion

The IR and Raman spectra of 3,5-dichlorosalicylic acid have been recorded and analyzed. The harmonic vibrational wavenumbers were calculated theoretically using Gaussian03 software. Calculations were performed by the DFT level using the standard 6-31G\* and SDD basis. The calculated wavenumbers (SDD) agree well with the observed wavenumbers. The data obtained from vibrational wavenumber calculations are used to assign vibrational bands found in IR and Raman spectra of the studied molecule.

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