

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

C. YOHANNAN PANICKER¹, HEMA TRESA VARGHESE², K. RAJU³
and G. KRISHNAKUMAR³

¹Department of Physics, TKM College of Arts and Science, Kollam, Kerala (INDIA)

²Department of Physics, Fatima Mata National College, Kollam, Kerala (INDIA)

³Department of Physics, University College, Trivandrum, Kerala (INDIA)

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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 medicine¹. In addition to analgesic, antipyretic and anti-inflammatory properties, salicylates possess also some other actions that have been proved to be therapeutically beneficial^{2,3}. 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^{4,5}. Vibrational spectroscopic studies and SERS spectra have been reported for salicylic acid⁶, 3-aminosalicylic acid⁷, sodium salicylate⁸, 4-aminosalicylic acid

sodium salt dihydrate⁹, methyl salicylate¹⁰, 5-sulphosalicylic acid¹¹ and ethyl salicylate¹². 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⁻¹. 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 cm^{-1} .

Computational details :

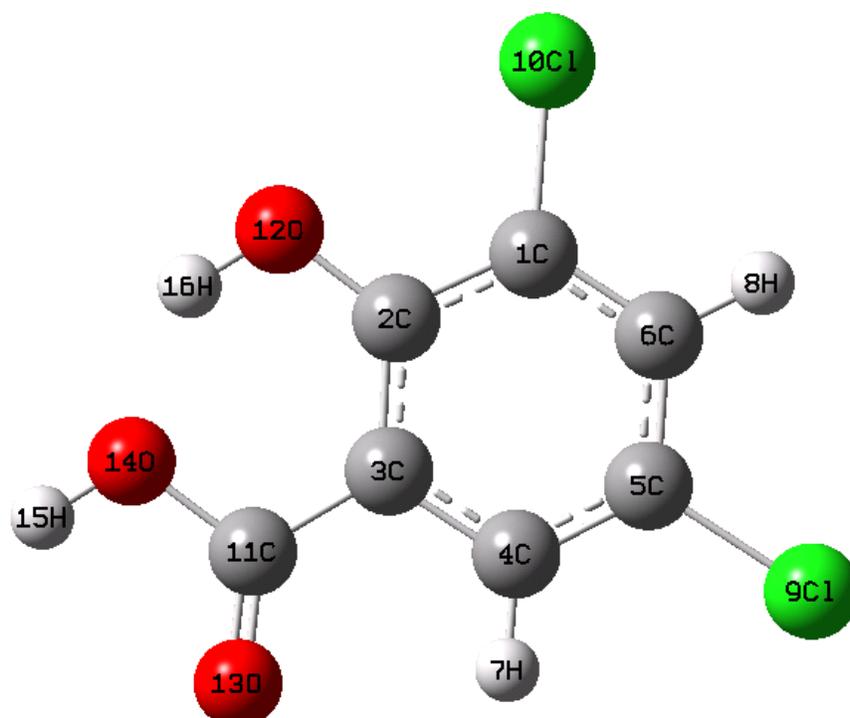
Calculations of the title compound were carried out with Gaussian03 software program¹³ using the B3LYP/6-31G* and B3LYP/SDD basis sets to predict the molecular structure and vibrational wavenumbers. Calculations were carried out with Becke's three parameter hybrid model using the Lee-Yang-Parr correlation 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 wavenumbers¹⁴. 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 C=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 cm^{-1} . The C=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 bonds¹⁵. C=O stretching¹⁶ vibration gives rise to a strong band in the region $1725\pm 65\text{ cm}^{-1}$. Rippon *et al.*¹⁷ reported a value of 1647 cm^{-1} for the carbonyl stretching mode. The band observed at 1668 cm^{-1} in the IR spectrum, 1695 in the Raman spectrum and at 1648 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 $1390\pm 55\text{ cm}^{-1}$. The C(=O)O stretching vibration, coupled to the OH in-plane deformation, exhibits a moderate to strong band in the region $1250\pm 80\text{ cm}^{-1}$. The DFT calculations give OH in-plane deformation at 1445 and C-O stretch at 1248 cm^{-1} . The out-of-plane deformation¹⁸ γOH exhibits a moderate band in the region $905\pm 65\text{ cm}^{-1}$. The C=O in-plane deformation is weakly to moderately active in the region $725\pm 95\text{ cm}^{-1}$. Most carboxylic acid display $\gamma\text{C}=\text{O}$ in the region $595\pm 85\text{ cm}^{-1}$ 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 $445\pm 125\text{ cm}^{-1}$. The C=O deformation bands are identified assigned (Table 1).



The SDD calculations give the OH stretching bands at 3327 cm^{-1} . The in-plane deformation¹⁶ is expected in the region $1400\pm 40\text{ cm}^{-1}$ and the band at 1359 cm^{-1} in the IR spectrum is assigned as the in-plane deformation of OH band. The calculated value is 1350 cm^{-1} . The stretching mode of the hydroxyl group with respect to the phenyl moiety C-O appears at 1229 cm^{-1} in the IR spectrum, 1232 cm^{-1} in the Raman spectrum and the calculated value are 1223 cm^{-1} . This band is expected in the region^{19,20} $1220\pm 40\text{ cm}^{-1}$. El-Shahway *et al.*²¹ reported C-O stretching at 1240 cm^{-1} .

The aromatic CH stretching vibrations¹⁶ 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 cm^{-1} are good group vibrations¹⁶. 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 regions¹⁶. In the case of C=O substitution, the band near 1490 cm^{-1} can be very weak¹⁶. 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 deformation¹⁶. The sixth ring stretching vibration, the ring breathing

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

B3LYP/6-31G*			B3LYP/SDD			IR ν (cm^{-1})	Raman $\nu(\text{cm}^{-1})$	Assign ments
ν (cm^{-1})	IR _I	R _A	ν (cm^{-1})	IR _I	R _A			
3500	85.64	209.70	3533	101.92	180.06	3416		νOH
3312	316.11	99.53	3327	327.61	98.10	3406		νOH
3132	0.81	75.37	3124	1.06	70.91	3095	3096	νCH
3131	6.01	31.72	3122	4.85	28.58	3074	3076	νCH
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	νPh
1547	6.04	10.63	1538	4.57	15.03			νPh
1466	106.19	5.74	1445	112.68	7.18	1449	1433	δOH
1412	102.02	1.82	1394	100.30	1.99		1383	νPh
1360	69.35	3.14	1350	41.65	4.01	1359		δOH
1306	93.60	29.81	1292	135.83	35.01	1299	1308	νPh
1271	141.58	6.38	1248	113.15	7.69	1267	1269	νCO
1244	144.57	4.65	1223	169.30	4.55	1229	1232	νCO
1201	125.72	14.35	1186	130.21	12.33	1186	1177	δCH
1128	101.07	11.40	1114	94.22	13.03	1098	1100	νPh
1089	11.94	6.42	1074	14.68	7.96			δCH
1033	148.76	20.44	1007	143.02	23.02			νPh
938	6.75	0.88	929	9.03	1.09		923	γCH
909	19.56	0.34	894	19.37	1.39	894	892	γCH
850	22.03	14.06	834	24.08	14.57	835	850	νCC
797	17.32	7.18	784	16.52	7.67	793	790	γOH
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		γOH
698	92.27	6.38	687	86.31	7.30		697	νCCl
672	84.07	1.18	673	48.82	0.19	650		νCCl
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			δPh
580	157.31	6.64	567	155.88	3.62	562		γPh
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	δCCl

345	0.95	0.07	338	0.94	13.95	336	δCCl
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	γCCl
177	0.78	2.65	174	0.73	2.84	170	γCCl
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

ν -stretching; δ -in-plane deformation; γ -out-of-plane deformation; t-torsion; Ph-phenyl ring; IR_I-IR intensity; R_A-Raman activity; X-substituent sensitive.

mode appears as a weak band near 1000 cm⁻¹ 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 νPh are expected in the region¹⁶ 1620- 1200 cm⁻¹ 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⁻¹ (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⁻¹, respectively¹⁶. These bands are also identified and assigned (Table 1).

The aliphatic CCl bonds absorb²⁰ at 830-560 cm⁻¹ and putting more than one chlorine on a carbon atom raises the CCl wavenumber. The CCl₂ stretching mode is reported at around 738 cm⁻¹ for dichloromethane and scissoring mode^{19,20} δCCl_2 around 284 cm⁻¹. For 2-cyanophenylisocyanide dichloride the νCCl stretching mode is reported

at 870 cm⁻¹ (IR), 877 (Raman) and at 882 cm⁻¹ theoretically²². Arslan *et al.*²³ reported νCCl at 683 cm⁻¹ (experimentally) and at 711, 736, 687, 697 cm⁻¹ theoretically. The deformation bands of CCl are reported²³ at 431, 435, 441 and 443 cm⁻¹. In the present case the bands at 687, 673 (SDD), 650 (IR) and 697 cm⁻¹ (Raman) are assigned as νCCl bands. The deformation bands of the CCl are assigned below 400 cm⁻¹.

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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