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Vibrational spectroscopic study of Salicylohydrazide

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Abstract

IR and Raman spectra of Salicylohydrazide 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, salicylate, hydrazone, IR, Raman

Introduction

Derivatives of Salicylates are widely used in medicine[1]. Hydrazones and their metal complexes possess pronounced biological and pharmaceutical activities as anti tumor[2-4], antimicrobial[5], anti tuberculosis[6] and anti malarial agents[7]. Hydrazones play an important role in improving the anti tumor selectivity and toxicity profile of anti tumor agents by forming drug carrier systems employing suitable carrier proteins[8]. They are also employed as extracting agents in spectrophotometric determination of some ions[9-11] and of some species in pharmaceutical formulations, as well as uses in catalytic processes[12,13] and waste water treatment[14]. Hydrazones, such as pyridoxyl isonicotinoylhydrazone, salicylaldehydebenzoylhydrazone and 2-pyridyl carboxaldehyde-2-thiophene carboxaldehyde hydrazone, act as orally effective drugs for the treatment of iron overload diseases or genetic diseases[15,16]. Metal complexes of hydrazone have found applications in various chemical processes like non linear optics, sensors etc.[17]. In the present study, the FT-IR, FT-Raman spectra of salicylohydrazine are analyzed experimentally and theoretically.

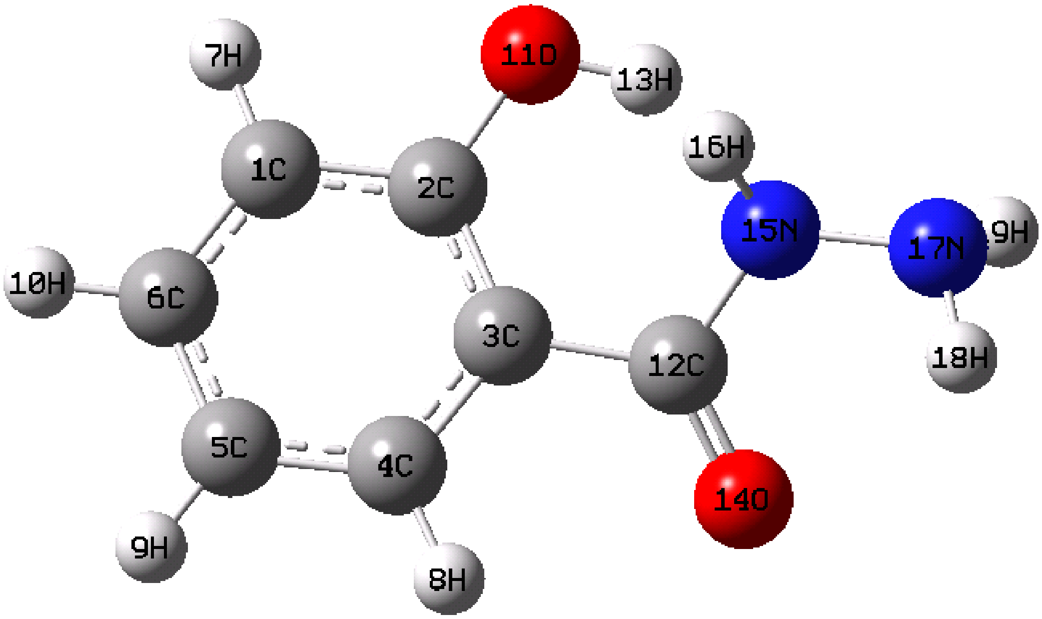
Experimental

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 program[18] 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[19]. 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 and Raman bands and calculated (scaled) wavenumbers and assignments are given in Table 1. The carbonyl group vibrations give rise to characteristic bands in the vibrational spectra. The intensity of these bands can increase owing to conjugation or formation of hydrogen bonds. In the present case the stretching mode of C=O is assigned at 1630 cm^{-1} in the IR spectrum and the SDD calculations give this mode at 1606 cm^{-1}. The deformation bands are observed at 666, 556 cm^{-1} in the IR spectrum, 666 cm^{-1} in the Raman spectrum and at 643, 541 cm^{-1} theoretically (SDD). In the case of 2-aminopyrazine-3-carboxylic acid[20] the vibrational modes of carboxylic group were assigned to the observed frequencies as follows: torsional C=O 101 cm^{-1} (Raman), 111 (HF); rocking C=O 537 (Raman), 571 (HF); wagging C=O 723 (Raman), 736 (HF); bending C=O 912 (Raman), 886 (HF); stretching mode C=O 1718 (Raman), 1786 cm^{-1} (HF).

The N-H stretching vibrations generally give rise to bands[21,22] at 3500-3300 cm^{-1}. In the present study, the NH stretching band split into a doublet, 3320, 3269 cm^{-1} in the IR spectrum owing to Davydov coupling between neighbouring units. A similar type of splitting observed in acetanilide[23] and N-methylacetamide[25] in the stretching band is also attributed to Davydov splitting. Furthermore, the NH stretching frequency is red shifted by 86 cm^{-1} in the IR spectrum with a strong intensity from the computed frequency, which indicates the weakening of the NH bond[26]. In mono-substituted amides, the in-plane bending frequency and the resonance stiffened CN band stretching frequency fall close together and therefore interact. The CNH vibration where the nitrogen and the hydrogen move in opposite directions relative to the carbon atom involves both NH bend and CN stretching and absorbs[27] at 1500 cm^{-1}. This band is very characteristic for mono substituted amides. The CNH vibration where N and H atoms move in the same direction relative to the carbon atom gives rise to a weaker band[27] near 1250 cm^{-1}. In the present case the bands observed at 1462, 1306 cm^{-1} in the Raman spectrum, 1466, 1302 cm^{-1} in the IR spectrum and 1449, 1300 cm^{-1} (SDD) are assigned as CNH bending modes. The out-of-plane NH wag is assigned at 779 cm^{-1} theoretically. Mary *et al.*[28] reported the NH bands at 1537, 1250, 650 cm^{-1} in the IR spectrum and at 1580, 1227, 652 cm^{-1} theoretically, for a similar derivative.

The NH_2 asymmetric stretching vibrations[29] give rise to a strong band in the region 3390 ± 60 cm^{-1} and the symmetric NH_2 stretching in the region 3210 ± 60 cm^{-1} with a some what weaker intensity. The DFT calculations give these modes at 3475 and 3426 cm^{-1} as $\upsilon_{as}NH_2$ and $\upsilon_{s}NH_2$ respectively. Baran *et al.*[30] reported $\upsilon_{as}NH_2$ at 3381, 3186 and 3398, 3203 cm^{-1} respectively for copper complexes of L-asparagine and L-glutamine. The NH_2 deformation band[20] δNH_2 is expected in the region 1610 ± 30 cm^{-1}. Most primary amides[29] display this δNH_2 band at 1610 ± 20 cm^{-1}. For the title compound, the δNH_2 band is observed at 1649 cm^{-1} in IR, 1645 cm^{-1} in Raman and at 1660 cm^{-1} theoretically. δNH_2 is reported at

1680 (IR), 1694 (Raman) and 1664 (IR), 1695 cm^{-1} (Raman) for metal complexes of L-asparagine and L-glutamine[30]. The in-plane NH_2 rock absorbs weakly to moderately in the region[29] 1125 ± 45 cm^{-1}. For L-glutamic acid 5-amide, ρNH_2 is reported at 1136 (IR), 1133 (Raman) and 1134 cm^{-1} theoretically[31]. The band at 1164 (IR), 1171 (Raman), 1164 cm^{-1} (SDD) are assigned to ρNH_2 for the title compound. The amide band, absorbing in the region 775 ± 45 cm^{-1}, is assigned to NH_2 out-of-plane twist and wagging mode ωNH_2 is expected in the region[29] 670 ± 60 cm^{-1}. The NH_2 wag is usually clearly separated from the twist and is easy to recognize by its broad band structure. The out-of-plane twist τNH_2 is observed at 796 cm^{-1} in the IR spectrum, 802 cm^{-1} in the Raman spectrum and at 798 cm^{-1} theoretically. The wagging mode ωNH_2 is assigned at 735 in IR spectrum and at 743 cm^{-1} theoretically (SDD) for the title compound. The wagging mode ωNH_2 is reported at 669, 675 (IR) and 663, 645 cm^{-1} (Raman)[31,32]. For Cd(II) and Hg(II) thiosemicarbazone complexes[33] bands in the region 3254-3409 cm^{-1} and 3231-3367 cm^{-1}, are attributed to asymmetric and symmetric NH_2 stretching vibrations. For para dimethylaminobenzaldehyde semicarbazone[34] NH_2 stretching vibration appears at 3466 cm^{-1} and 3415 cm^{-1} and NH stretching vibration appears at 3230 cm^{-1}.

The C-N stretching vibration[29] coupled with the δNH, is active in the region 1275 ± 55 cm^{-1}. El-Shahawy *et al*[35] observed a band at 1320 cm^{-1} in the IR spectrum as this υC-N mode. In the present case, the bands at 1240 cm^{-1} in the IR spectrum and at 1241 cm^{-1} (SDD) is assigned as thise mode. υN-N has been reported at 1151 cm^{-1} by Crane *et al.*[36], 1121 cm^{-1} by Bezerra *et al.*[37] and 1130 cm^{-1} by El-Behery and El-Twigry[38]. In the present case, the band at 1146 (IR), 1155 (Raman), 1151 cm^{-1} (SDD) is assigned to the υN-N mode. υN-N is reported in the range 1037-1083 cm^{-1} for copper (II) complexes of thiosemicarbazones[39].

The SDD calculations give the OH stretching band at 3442 cm^{-1}. The in-plane deformation[29] is expected in the region 1400± 40 cm^{-1} and the band at 1353 cm^{-1} in the IR spectrum is assigned as the in-plane deformation of OH band. The calculated value is 1338 cm^{-1}. The stretching mode of the hydroxyl group with respect to the phenyl moiety C-O appears at 1263 cm^{-1} in the IR spectrum, 1268 cm^{-1} in the Raman spectrum and the calculated value are 1271 cm^{-1}. This band is expected in the region[27, 40] 1220 ± 40 cm^{-1}. El-Shahway *et al.*[35] reported C-O stretching at 1240 cm^{-1}.

For 1,2-disubstituted benzenes, the CH stretching modes[29] of the ring are expected in the region 3110-3000 cm^{-1}. The calculated (SDD) values are 3120, 3111, 3095, 3081 cm^{-1}. These vibrations are observed at 3141, 3068, 3026 cm^{-1} in the IR spectrum and at 3100, 3063 cm^{-1} in the Raman spectrum. The bands observed at 1588, 1534, 1440, 1302, cm^{-1} in the IR spectrum and 1588, 1540, 1441, 1410, 1306 cm^{-1} in the Raman spectrum are assigned to the ring stretching modes υPh. The calculated

Table 1. Calculated vibrational wavenumbers, measured IR and Raman bands and assignments

B3LYP/6-31G*			B3LYP/SDD			IR υ (cm^{-1})	Raman υ(cm^{-1})	Assignments
υ (cm^{-1})	IR$_I$	R$_A$	υ (cm^{-1})	IR$_I$	R$_A$			
3454	4.27	72.26	3475	6.91	59.48			υ$_{as}$NH$_2$
3425	28.25	46.00	3442	118.63	86.60			υOH
3409	124.16	100.02	3426	49.14	59.97			υ$_s$NH$_2$
3344	2.07	136.06	3355	2.18	126.83	3320 3269	3323	υNH
3117	8.71	225.93	3120	12.73	231.62	3141		υCH
3110	10.22	44.98	3111	12.37	38.38		3100	υCH
3096	10.23	97.15	3095	7.74	69.42	3068		υCH
3081	5.02	66.78	3081	4.41	47.04	3026	3063	υCH
1685	16.57	22.12	1660	21.08	18.50	1649	1645	δNH$_2$
1625	122.49	10.72	1606	78.44	18.29	1630		υC=O
1608	161.33	100.16	1589	247.51	107.75	1588	1588	υPh
1566	17.13	7.85	1555	18.09	9.72	1534	1540	υPh
1474	21.59	1.81	1449	27.36	2.48	1466	1462	δNH
1465	78.25	3.12	1438	86.59	3.82	1440	1441	υPh
1424	120.32	4.21	1401	110.10	4.29		1410	υPh
1349	10.99	5.23	1338	8.03	8.16	1353		δOH
1313	28.78	2.73	1300	29.90	2.80	1302	1306	υPh, δNH
1293	17.52	7.46	1271	27.04	9.91	1263	1268	υCO
1258	167.98	67.03	1241	146.08	61.41	1240		υCN
1232	11.75	7.60	1218	11.42	9.16			δCH
1181	140.74	3.29	1164	74.33	1.80	1164	1171	ρNH$_2$
1173	25.18	3.77	1161	80.86	6.38			δCH
1163	46.95	10.49	1151	55.41	11.21	1146	1155	υNN
1094	0.52	2.09	1077	1.18	1.62	1067	1086	δCH
1054	4.97	15.70	1037	6.20	23.79	1036	1039	υPh
1019	9.64	9.29	1001	14.68	10.06		1000	δCH
987	0.36	0.06	996	0.50	0.03	989		γCH
961	2.07	0.69	968	2.81	0.15	965	963	γCH
882	37.58	2.70	879	1.73	0.58	882	891	υCC
875	11.56	5.02	863	53.26	3.35	860		γCH
821	6.32	7.83	798	3.21	10.18	796	802	τNH$_2$

807	79.94	1.63	792	84.89	2.86			γOH
793	15.81	5.33	779	52.05	1.78			γNH
764	185.67	6.54	758	100.27	0.99	761	762	γCH
755	42.55	5.76	743	124.26	10.59	735		ωNH_2
693	12.45	1.97	690	17.37	1.09		669	γPh
658	5.23	6.31	643	5.10	7.82	666	666	δC=O
551	4.81	8.27	541	5.25	6.96	556		γC=O
537	13.91	3.32	528	12.29	6.21	531		δCCN
514	6.26	2.84	504	10.53	3.00	512	516	γPh(X)
455	139.08	4.46	449	115.52	3.98		446	δPh(X)
445	72.50	3.09	435	77.74	3.82	428		γPh
372	12.39	2.63	363	10.65	2.85		377	γPh(X)
328	7.77	4.50	318	11.99	4.34			δPh(X)
298	33.25	3.39	288	33.07	3.31		271	γPh(X)
265	3.11	2.89	259	3.97	1.87		245	tNH
214	7.80	1.78	210	2.87	1.25		209	tNH2
190	15.04	8.70	180	18.50	7.36		163	tCCN
149	1.29	1.50	139	1.43	1.40			tCOH
104	5.19	1.89	105	4.10	1.68			tPh
72	6.58	1.66	68	6.19	1.70			tPh

υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; ρ-rocking; ω-wagging; τ-twisting; t-torsion; Ph-phenyl ring; as-asymmetric; s-symmetric; X-substituent sensitive.

values (SDD) for these modes are 1589, 1555, 1438, 1401, 1300, cm^{-1}. These vibrations are expected in the range[29] 1620-1260 cm^{-1}. For 1,2-disubstituted benzenes δCH modes are seen in the range[29] 1300-1240 and 1170-1010 cm^{-1}. The calculated values are 1218, 1161, 1077, 1001 cm^{-1}. The experimental values are 1067, cm^{-1} in the IR spectrum and at 1086, 1000 cm^{-1} in the Raman spectrum. In ortho disubstitution the ring breathing mode has three frequency intervals according to whether both substituents are heavy, or one of them is heavy while the other is light, or both of them are light. In the first case, the interval is 1100-1130 cm^{-1}, in the second case 1020-1070 cm^{-1}, while in the third case it is between[40] 630 and 780 cm^{-1}. The SDD calculations give 1037 cm^{-1} as ring breathing mode for phenyl ring. The experimental values are 1036 (IR) and 1039 cm^{-1} (Raman).

The out-of-plane CH deformation bands γCH are expected[29] in the region 995-720 cm^{-1}. As seen from the Table 2, the SDD calculations give wavenumbers at 996, 968, 863, 758 cm^{-1}. The bands at 989, 965, 860, 761 in IR and at 963, 762 cm^{-1} in Raman spectrum are assigned to this mode. According to Roeges[29], in the case of 1,2-disubstitution only one strong absorption in the region 755± 35 cm^{-1} is observed, and is due to γCH mode. This is confirmed by the presence of a strong γCH at 761 cm^{-1} in the IR spectrum and is supported by the computational result at 758 cm^{-1}. The substituent sensitive modes of the phenyl rings are also identified and assigned (Table 1).

Conclusion

The IR and Raman spectra of Salicylohydrazide were recorded and analyzed. The wavenumbers were calculated theoretically using Gaussian03 software package. The observed wavenumbers were found to be in agreement with calculated (SDD) values.

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