Computational study of Nitrate and Chloride based 4-Carboxyaniline single crystal

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Abstract

Full geometry optimizations of 4-Carboxyaniline, 4-Carboxyanilinium Nitrate and 4-Carboxyanilinium chloride have been carried out without imposing any constraint using Gaussian 09 program package. The experimental FT-IR and FT-Raman spectra of the title compounds had been taken from the literature in the region (4000-500) cm^{-1}. The observed frequencies of the spectra were scaled using scale factor yielding good agreement between observed and calculated frequencies. Theoretical calculations were performed in order to study the optimized conformation, polarizability and electrostatic potential distribution of the three compounds using DFT. TD-DFT calculation had been carried out to investigate the adsorption spectra and HOMO-LUMO energies.

Keywords: *DFT, Vibrational spectra, HOMO, LUMO, MESP*

I. Introduction

4-Aminobenzoic acid is an important biological molecule. It is also called as vitamin B_x, which is an essential nutrient for some bacteria [1]. PABA acts as a bacterial cofactor involved in the synthesis of folic acid. It is a starting material in the synthesis of target esters, salts, azo dyes and many organic compounds and also used in medicine for preparing local anaesthetics, ointments and helps to protect the skin from sunburn and cancer [2]. p-Carboxyaniline play an important role in pharmaceutical field to relieve the pain from headaches and nervous states [3,4]. In 1989 Etter & Frankenbach proved that PABA is suitable for structure extension through linear hydrogen bonding associations through both the carboxylic acid and amine functional groups. This kind of property was helpful for promoting the design of noncentrosymmetric organic materials co-crystallization. In our systematic investigation, PABA based three structures such as 4-Carboxyaniline (Athimoolam & Natarajan, 2007), 4-Carboxyanilinium Nitrate (Athimoolam & Natarajan, 2006) and 4-Carboxyanilinium chloride (Li-Jun Han et. al., 2011) have been already studied to understand their structure extension properties. But to the best of our knowledge, there is no computational work for the title compounds. So, theoretical attempt was made on nitrate and chloride based 4-Carboxyaniline single crystal to determine a relationship between some quantum chemical parameters obtained from the structure of the compounds. IR, Raman, UV and NMR spectra is recorded and compared with previous studies. These results are discussed and summarized in the present work.

II. Computational Details

The molecular structure of the compounds 4-Carboxyaniline, 4-Carboxyanilinium Nitrate and 4-Carboxyanilinium chloride were fully optimized and the structural parameters have been computed by using Gaussian09 program. The optimized molecular structures of these compounds were calculated using B3LYP method with 6-311G level of basis set. The structural parameters of 4-Carboxyaniline, 4-Carboxyanilinium Nitrate and 4-Carboxyanilinium chloride obtained from the DFT method. Theoretically optimized bond lengths and angles are larger than the experimental ones since the theoretical calculations were done assuming isolated molecule in gaseous phase. For each compound vibrational frequencies were calculated at B3LYP/6-311G level and were scaled by a factor 0.966.

III. Quantum Chemical Calculations

Quantum chemical calculations to be done for 4-Carboxyaniline, 4-Carboxyanilinium Nitrate and 4-Carboxyanilinium chloride using DFT calculations and three compounds are compared with the results of previous studies [5,6,7].

A. Molecular geometries

The optimized molecular structures of the title compounds with atomic labeling are shown in Fig. 1. The title compounds represent a part of our research into intermolecular interactions in hydrogen bonded ionic crystals of acid salts.

a) 4-Carboxyaniline

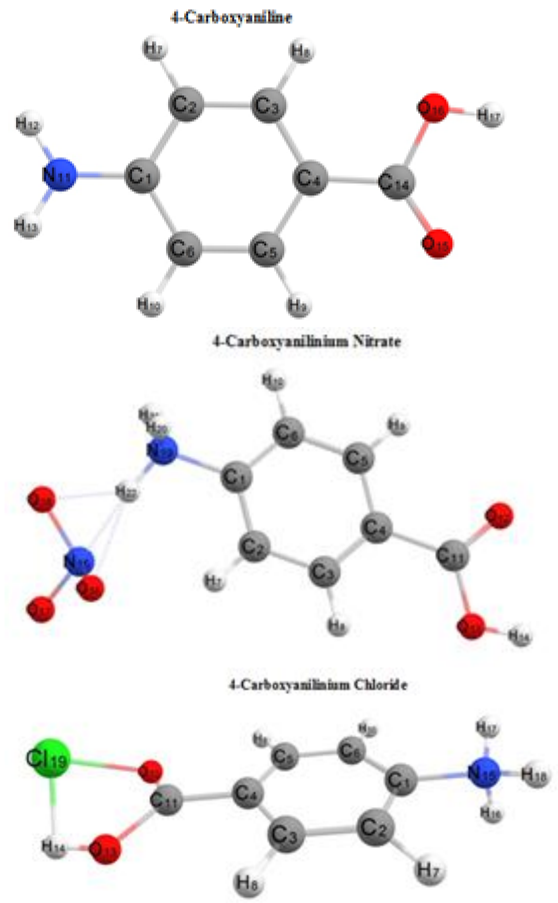
The position of N-bound H atoms [R(11,12) and R(11,13)] was found to be 0.91 Å. The hydroxyl H atom (O16-H17) was fixed at the position of 0.96 Å. Dominik Cincic and Branko Kaitner (2008) reported the hydrogen atoms bound to carbon atoms were treated as riding, with C-H=0.93 (aromatic) or 0.96 Å (methyl). The bond length of C2-H7, C3-H8, C6-H10 and C5-H9 has the same value of 1.099Å. It shows that very nearly same amount of o-quinone contribution as of p-quinone contribution in the present compound. The C4-C14 distance is slightly longer. The C1-N11 (1.54Å) bond distance is significantly larger than the corresponding C-N bond (1.408Å) at the β-polymorph of the 4-aminobenzoic acid [8] and also its bond distance value (1.372Å) reported by S.Athimoolam and S.Natarajan, 2006. The obtained C14-O15 bond length is 1.2273Å. It is found that the C-O bond is exactly same with the experimental result. The C-H, N-H and O-H values are somewhat shorter than the standard values for inter nuclear separations. The crystal structure indicates that twinning and disorder are common. The carboxyl and amino groups are slightly interchanged from the plane of benzene rings and the nitrogen atoms are non-planar.

b) 4-Carboxyanilinium Nitrate

4-aminobenzoic acid has both a carboxyl group and an amino group. A strong O16-H22-O18 hydrogen bond links the 4-aminobenzoic acid cation to nitrate anion. N15-O16, N15-O17, N15-O18 bond lengths for the nitrate anion is 1.36Å. Bond angle value (109.4712Å) of O16-N15-O18, O16-N15-O17, O17-N15-O18 is found to be small as compared to the value of 118.93Å reported by Asath Bahadur et. al., 2007. N15-H22-O18 and O16-H22-O18 hydrogen bonds stabilize the crystal structure. All the oxygen atoms are involved in the hydrogen bonding network. A short interatomic contact (0.91Å) is observed in C11-O13, C11-O12. The small value of O16-O17 (0.96Å) is a consequence of the dense packing of the components by the hydrogen bonding.

c) *4-Carboxyanilinium chloride*

In this compound, the carboxyl H atom participates in hydrogen bonding with a neighbouring anion through an O13-H14…Cl19 hydrogen bond. This crystal structure is stabilized by N-H…O and N-H…Cl hydrogen bonds. The bond length of C1-N15 is 1.47 Å. In the case of 4-Carboxyanilinium chloride (L.-J. Han, S.-P. Yang, X.Tao and Y.-F. Ma, 2011) and 4-Carboxyanilinium (2R,3R) tartrate single crystal (Athimoolam & Natarajan, 2007), the amine group is protonated and the values of C-N bond lengths are 1.471Å and 1.464Å. All H atoms were located in the structure; C-H=1.07Å, N-H=1.0Å and O-H=0.96Å. The carboxyl bond distances C11-O12 and C11-O13 are 1.2584Å and 1.43Å respectively. The observed C-C bond length is 1.4014Å.


4-Carboxyaniline

4-Carboxyanilinium Nitrate

4-Carboxyanilinium Chloride

Fig 1: Optimized molecular structures of the 4-Carboxyaniline, 4-Carboxyanilinium Nitrate and 4-Carboxyanilinium Chloride with atomic labeling

B. Vibrational spectra

a) 4-Carboxyaniline

Fig. 2 shows the IR and Raman spectra of 4-carboxyaniline compound. The 4-carboxyaniline molecule contains para substituted aromatic ring, NH2 and carboxylic acid functional groups. The theoretically analysed IR and Raman spectra are compared with the experimental data reported by C.Muthuselvi et. al., (2017). The corresponding IR and Raman frequency assignments are listed in Table I. The antisymmetric and symmetric stretching vibrational mode of C=O have wavenumbers in the region 1688 cm^{-1} and 1635 cm^{-1} respectively [9]. The C-O stretching mode of carboxylic group normally occurs in the vibrational region of 1320–1210 cm-1 [10]. But C-O stretching mode of the compound has wavenumbers at 1271 cm^{-1}, 1242 cm^{-1}. The O–H stretch from CO–OH group is identified at 3080 cm^{-1}. The O–H group out-of plane bending wavenumber appears at 917 cm^{-1}. Benzene ring C-H stretching mode is observed at 3080 cm^{-1}. The C–H in–plane bending is seen in the region of 1185, 1132 cm^{-1}. The C-H out –of –plane bending vibrations are at 750, 681 cm^{-1}. The C=C stretching modes occur in the region 1599 and 1564 cm^{-1} [11]. The C-C stretching mode is observed at 1271 cm^{-1}. The C-N stretching mode is at 1242 cm^{-1}. The ring breathing mode is identified at 815 cm^{-1}. The NH$_2$ symmetric and antisymmetric stretching mode of aniline is normally expected in the region of 3480-3250 cm^{-1} [11,12]. In the present work, symmetric stretching of NH$_2$ presents at 3202 cm-^{1} and antisymmetric stretching at 3297 cm^{-1}. And also the wagging mode of aniline is found in the range of 545 cm^{-1} [13].

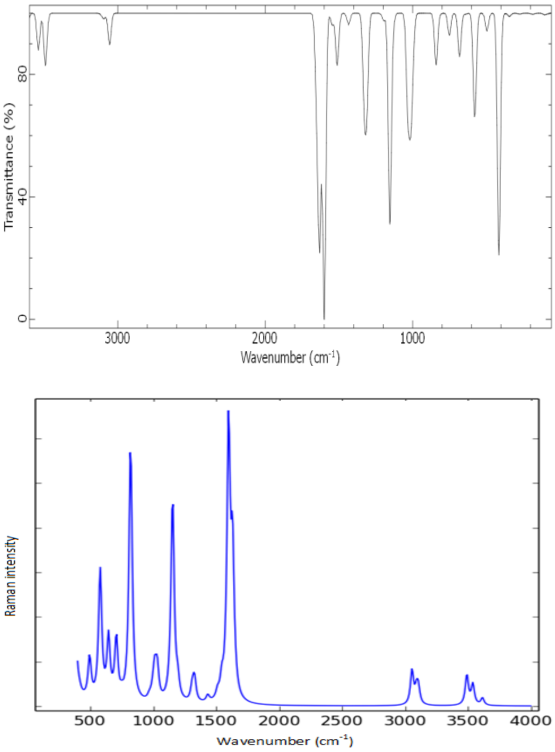


Fig 2: IR and Raman spectra of the 4-Carboxyaniline

b) 4-Carboxyanilinium Nitrate

Fig. 3 shows the IR and Raman spectra of 4-Carboxyanilinium nitrate. The title compound has four functional groups such as para substituted benzene ring, -[NH$_3$]$^+$, -COOH and NO$_3^-$. The detailed frequency assignment of the compound is listed in Table II. The bands observed at 2942 cm^{-1} and 2979 cm^{-1} was assigned to C-H stretching mode. Usually C=C stretching mode was observed in the region of 1650-1430 cm^{-1}. The C=C stretching mode was assigned at 1505 and 1566 cm^{-1}. The antisymmetric and symmetric stretching mode of C=O have wavenumbers in the range 1632 cm^{-1} and 1596 cm^{-1} respectively. The C-O stretching mode of carboxylic group occurs in the vibrational range of 1192 and 1240 cm^{-1}. The antisymmetric and symmetric stretching mode of -[NH$_3$]$^+$ group normally expected to fall in the region of 3200 and 2800 cm^{-1}. The antisymmetric stretching mode of -[NH$_3$]$^+$ group appears at 2979 cm^{-1} and also symmetric stretching mode is at 2857 and 2942 cm^{-1}. The -[NH$_3$]$^+$ twisting mode was observed as a weak peak at 454, 511 cm^{-1}. The -[NH$_3$]$^+$ wagging mode is observed as weak bands at 941 cm^{-1}. The -[NH$_3$]$^+$ rocking mode is found at 1083, 1103 cm^{-1}. The in-plane bending of O-H group appears at 1403 cm^{-1}, 1311 cm^{-1}, 1103 cm^{-1} and 1083 cm^{-1}. The planar [NO$_3$]$^-$ ion shows four fundamental modes such as antisymmetric stretching, symmetric stretching, out-of-plane bending and in-plane-bending. The antisymmetric stretching mode of [NO$_3$]$^-$ group is found at 1330 cm^{-1}. The out-of-plane bending of [NO$_3$]$^-$ group were observed at 829 cm^{-1}, 797 cm^{-1} and 749 cm^{-1}. And also in-plane-bending was appeared at 692 cm^{-1}. The symmetric stretching mode of [NO$_3$]$^-$ group was recorded in the present case at 1008 cm^{-1} and 986 cm^{-1}.

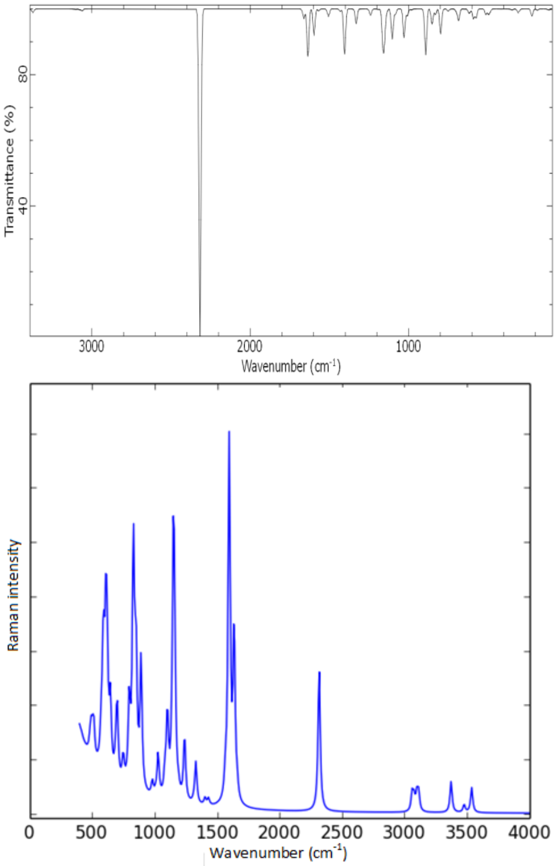


Fig 3: IR and Raman spectra of the 4-Carboxyanilinium Nitrate

c) 4-Carboxyanilinium chloride

Fig. 4 shows the IR and Raman spectra of 4-carboxyanilinium chloride. The IR and Raman assignments are given in Table III. The symmetry stretching and bending modes of NH$_3^+$ group are doubly degenerate [7] and also both the modes are IR and Raman active. The NH$_3^+$ group gives rise to the internal modes of vibrations such as asymmetric stretching, symmetric stretching, the anti-symmetric planar deformation (rocking), and the anti-symmetric non-planar deformation (torsion). For the NH$_3^+$ group, the asymmetric and symmetric stretching modes are reported in the region of 1518, 1489 cm^{-1} and 2955 cm^{-1} respectively. And also NH$_3^+$ group of torsion mode is observed at 414, 581 cm^{-1}. Rocking mode of it occurs at and 830, 1155 cm^{-1}. The aliphatic monocarboxylic acids generally exhibit due to in plane vibration of the O-C=O group which is determined in the region 665-610 cm^{-1}. The O-H stretching in the carboxylic group is appeared in very strong band at 3136, 3334 and 3358 cm^{-1}. The O-H stretching in the lower band is observed in the frequencies at 516 cm^{-1}. Normally in biological crystals, O-H-O hydrogen bonds are relatively stronger than N-H-O bonds. In the present structure, the O-H-O and N-H-O stretching is found at 2727 and 3136 cm^{-1} respectively. COO$^-$ rocking is identified at 454 cm^{-1} and COO$^-$ wagging is at 581 cm^{-1}. For the title molecule, C-N symmetry stretching mode is assigned at 1303, 1321 cm^{-1}.

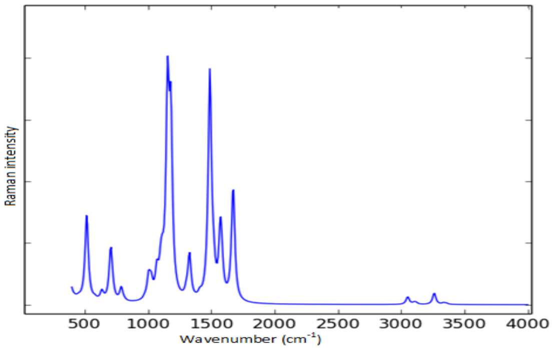


Fig 4: IR and Raman spectra of the 4-Carboxyanilinium Chloride

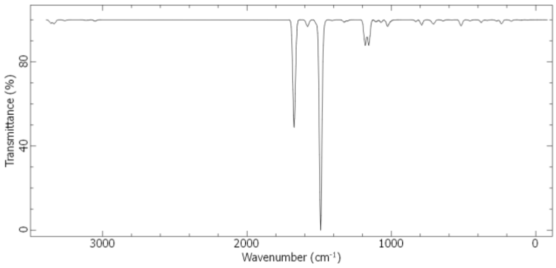


Table I

Detailed assignment of fundamental vibrations of 4-carboxyaniline

No	**Symmetry Species C_S**	**Experimental frequency [Ref 5]**		**Calculated using B3LYP/6-311G method**			**Characterization of normal modes**
		IR	**Raman**	**Scaled Frequency (cm^{-1})**	**IR intensity**	**Raman activity**	
1	A"			82.2461	0.7445	0.9722	
2	A"		103	104.103	2.3925	0.8284	Lattice vibration modes
3	A'		192	184.883	1.6591	0.38	
4	A"		282	273.065	1.2551	0.3203	
5	A'		352	343.1	4.4052	6.217	C-C-C-C Out of phase deformation
6	A'		381	371.428	0.3991	0.2996	
7	A"			387.644	0.4224	1.2068	
8	A"			414.459	344.3619	0.1221	
9	A"			418.19	0.7718	0.0325	
10	A'			494.512	13.6438	1.2818	
11	A"			496.513	11.7587	1.173	
12	A'	552		574.85	56.3448	1.2571	NH2 Wagging
13	A"			580.058	97.8747	9.7383	
14	A'			645.586	1.6745	6.523	
15	A"	696	639	681.37	62.0561	0.1392	C-H Out of plane bending
16	A'			707.568	0.7263	7.9204	
17	A"	770	767	750.89	31.5599	0.5795	C-H Out of plane bending
18	A"	843	846	815.66	0.4285	2.2242	Ring breathing
19	A'			821.341	1.4213	44.3886	
20	A"	893	--	840.497	73.2076	0.0563	O-H& C-H Out of plane bending
21	A"	928	--	967.418	0.0705	0.7749	O-H Out of plane bending
22	A"			978.708	0.2136	0.5173	
23	A'			998.447	49.3136	2.2335	
24	A'			1013.18	133.4829	8.569	
25	A'			1032.45	129.8709	9.8231	
26	A'	1173	1179	1132.42	13.0968	1.5595	C-H In plane bending
27	A'			1154.33	299.3796	80.9176	

28	A'	1211	--	1195.51	10.4805	7.165	C-H In plane bending
29	A'	1290	1284	1310.28	120.1655	6.1913	C-O & C-N Stretching
30	A'	1317	1312	1312.23	2.5273	1.4101	C-O & C-C Stretching
31	A'			1327.48	116.2472	12.0413	
32	A'	1420	--	1334.58	3.8006	1.221	O-H In plane bending
33	A'	1441	1433	1434.2	16.7087	4.4667	O-H In plane bending
34	A'	1570	--	1511.65	74.1578	5.5435	C=C Stretching
35	A'	1599	1601	1545.12	16.4201	13.8664	C=C Stretching
36	A'	1628	--	1598.95	433.6114	238.2207	C=O Symmetric stretching; NH2 Rocking
37	A'	1663	--	1630.78	314.6354	130.3639	C=O Antisymmetric stretching
38	A'			1650.08	118.2664	4.6797	
39	A'	2855	--	3055.01	21.8876	87.9702	O-H Symmetric stretching
40	A'	2924	--	3056.73	22.7229	97.8893	O-H Symmetric stretching
41	A'	3057	3044	3091.97	5.9402	74.8139	O-H Symmetric stretching ; C-H Stretching
42	A'	3364	3361	3105.92	3.1955	89.3111	NH2 Symmetric stretching
43	A'	3462	--	3491.54	74.674	256.0871	NH2 Antisymmetric stretching
44	A'			3539	52.6198	181.8005	
45	A'			3615.56	19.3079	70.7319	

Table II
Detailed assignment of fundamental vibrations of 4-carboxyaniinium nitrate

No	**Symmetry Species C_S**	**Experimental frequency [Ref 6]**		**Calculated using B3LYP/6-311G method**			**Characterization of normal modes**
		IR	**Raman**	**Scaled Frequency (cm^{-1})**	**IR intensity**	**Raman activity**	
1	A			18.7523	2.1101	3.1202	
2	A			32.1495	3.118	7.0104	
3	A			42.0987	0.1069	4.8204	
4	A			77.1309	0.726	1.4351	
5	A			79.5115	0.3521	0.937	
6	A		103	103.097	0.2949	0.815	Lattice vibration modes
7	A			115.267	7.0414	0.6438	
8	A		192	187.827	9.8422	0.6137	Lattice vibration modes
9	A		233	221.345	56.6798	5.4341	
10	A			307.813	30.4527	0.8469	
11	A		352	346.032	7.6501	2.6224	C-C-C-C Out of phase deformation
12	A		362	357.855	1.5308	0.5051	
13	A			415.453	0.4933	0.0694	
14	A	480	--	484.927	19.9613	0.6854	$[NH_3]^+$ Twisting
15	A			496.358	37.8727	1.3271	
16	A	530	--	512.835	41.6366	2.0024	$[NH_3]^+$ Twisting
17	A			574.009	71.744	2.1766	
18	A			590.837	75.6604	8.8056	
19	A			609.999	14.7535	9.1748	
20	A			619.78	27.3883	8.2346	
21	A			646.692	1.1293	6.1182	

22	A			684.394	86.8046	0.3487	
23	A	718	716	693.317	11.8317	1.5781	$[NO_3]^-$ In plane bending; C-H Out of plane bending
24	A			701.066	12.324	7.4029	
25	A	754	--	749.62	17.2718	3.2658	$[NO_3]^-$ Out of plane bending; C-H Out of plane bending
26	A	822	812	797.925	199.3079	11.1269	$[NO_3]^-$ Out of plane bending
27	A	847	834	830.577	39.6158	35.1234	Ring breathing mode; $[NO_3]^-$ Out of plane bending
28	A			837.827	4.6839	2.808	
29	A			852.261	119.3581	20.0633	
30	A	932	--	892.038	366.3534	23.3597	O-H Out of plane bending
31	A	964	--	982.232	6.4666	2.9914	$[NH_3]^+$ Wagging
32	A	1020	--	986.412	0.5962	0.2085	C-H In plane bending; Symmetric stretching of $[NO_3]^-$
33	A			1008.78	55.1696	0.8098	
34	A	--	1035	1029.17	228.7319	10.6568	C-H In plane bending; Symmetric stretching of $[NO_3]^-$
35	A	1123	--	1083.91	40.3549	6.1885	$[NH_3]^+$ Rocking; O-H In plane bending; C-H In plane bending
36	A	--	1131	1103.27	240.142	24.021	$[NH_3]^+$ Rocking; O-H In plane bending; C-H In plane bending
37	A	1159	1179	1139.76	22.4436	6.6611	C-H In plane bending
38	A			1152.61	198.6841	82.7151	
39	A			1162.33	268.2408	23.8235	
40	A	1235	--	1192.21	4.0575	2.4732	C-O Stretching
41	A	--	1251	1240.67	50.7087	25.7674	C-O Stretching
42	A	1324	1324	1312.21	0.9113	0.9213	C=C Stretching; C-O Stretching; C-N Stretching; O-H In plane bending
43	A	--	1343	1330.84	112.4277	19.063	C=C Stretching; Anti-symmetric stretching of $[NO_3]^-$
44	A			1337.48	4.9716	0.3412	
45	A	1412	1413	1404.34	360.513	3.7433	O-H In plane bending
46	A	1537	1528	1431.67	21.0324	3.7816	Symmetric bending of $[NH_3]^+$
47	A	--	1582	1506.17	60.5357	0.1785	C=C Stretching
48	A	1612	1611	1567.66	14.8572	14.2923	C=C Stretching; Anti-Symmetric bending of $[NH_3]^+$
49	A			1597.38	211.6707	262.1403	
50	A			1633.01	90.8619	43.230244	
51	A	1636	--	1636.82	303.59	128.2332	C=C Stretching; Symmetric stretching of C=O
52	A	1692	1690	1661.92	76.6644	8.7144	Anti-symmetric stretching of C=O
53	A			2317.32	2634.5138	279.0937	

54	A	--	2920	3061.68	14.1017	81.1083	Symmetric stretching of $[NH_3]^+$; O-H Stretching
55	A	--	3049	3076.28	5.23	61.9386	Symmetric stretching of $[NH_3]^+$; C-H Stretching; O-H Stretching
56	A	3069	3080	3099.6	2.7073	139.911575	Anti-symmetric stretching of $[NH_3]^+$; C-H Stretching
57	A			3113.18	0.8526	84.5962	
58	A			3372.89	28.193	191.2635	
59	A			3477.45	23.2429	54.006	
60	A			3537.77	62.1097	182.4999	

Table III
Detailed assignment of fundamental vibrations of 4-carboxyanilinium chloride

No	Symmetry Species C_S	Experimental frequency [Ref 7]		Calculated using B3LYP/6-311G method			Characterization of normal modes
		IR	Raman	Scaled Frequency (cm^{-1})	IR intensity	Raman activity	
1	A			-40.4146	0.0366	0.7209	
2	A			24.4728	0.4104	1.0363	
3	A			54.8122	1.7745	1.8829	
4	A			67.7698	0.5722	1.1921	
5	A		103	102.885	6.208	0.599	Lattice vibration modes
6	A		181	170.152	23.8499	5.2183	
7	A		251	238.35	67.1758	17.588	
8	A		282	272.421	21.3056	4.1643	
9	A		352	339.482	11.4375	3.6929	C-C-C-C Out of phase deformation
10	A		381	379.132	46.3221	6.7683	
11	A		437	416.25	0.2732	0.0188	$[NH_3]^+$ Torsion; COO^- Rock
12	A	497	477, 452	456.78	17.5359	0.532	
13	A	532	538	519.487	107.6254	40.587	O-H Stretching
14	A	572	582	584.171	2.0246	1.131	COO^- Wagging; $[NH_3]^+$ Torsion
15	A	654		639.8	0.2828	6.4099	O-C=O In plane deformation
16	A		663	645.306	19.3453	0.382	
17	A		737	709.997	73.7303	49.3333	C-O-H Torsion
18	A		757	725.402	21.5281	5.092	
19	A			793.817	92.6507	16.3095	
20	A	806	802	817.502	0.0284	1.2107	C-H Out of plane deformation
21	A		868,852	834.33	29.1962	0.0827	$[NH_3]^+$ Rocking; C-C Stretching;
22	A		1004	979.534	1.4197	3.6394	C-O Stretching
23	A	1024	1021	997.856	0.4671	0.1963	
24	A			1005.86	3.4289	1.0087	
25	A			1011	25.0774	44.8312	
26	A	1059	1067	1030.76	111.9607	33.9733	C-O Stretching
27	A			1076.27	41.8645	61.9948	
28	A			1105.66	6.9106	38.0245	
29	A	1108	1113	1109.86	23.6774	29.3793	C-O Stretching
30	A			1120.9	6.9813	50.4709	
31	A		1164	1160.9	449.3342	568.5014	-OH, $[NH_3]^+$ Rocking
32	A		1239,	1186.72	451.8409	497.9513	-OH In plane

			1224				deformation
33	A	1351		1309.1	18.6106	22.5453	C-N Symmetric stretching
34	A	1367		1327.68	7.7166	6.8195	
35	A			1334.63	35.8483	173.1841	
36	A	1469	--	1416.05	14.1101	21.6466	C-N Asymmetric stretching
37	A			1477.59	116.7866	34.7293	
38	A	1554	1552	1496.34	3741.4811	1193.7481	COO^- Asymmetric stretching; $[NH_3]^+$ Asymmetric deformation
39	A			1525.16	68.406	118.5313	
40	A			1578.48	11.6037	329.9798	
41	A	1588	1595	1588.36	112.3113	179.78	$[NH_3]^+$ Asymmetric deformation
42	A	1626	--	1672.7	127.8425	15.2672	$[NH_3]^+$ Asymmetric deformation
43	A			1676.78	374.4563	178.1767	
44	A			1681.8	1512.7423	646.4372	
45	A	3059	3077	3064.04	8.8725	97.9662	O-H Stretching; C-H Stretching; Symmetric stretching of $[NH_3]^+$
46	A			3065.21	16.1347	201.9093	
47	A			3116.06	5.0665	66.9536	
48	A			3130.91	8.4314	62.9646	
49	A	3250	--	3274.95	18.4194	558.1608	O-H Stretching; N-H…O Stretching
50	A	3410		3349.29	75.1484	82.9203	O-H Stretching
51	A	3483	--	3373.39	59.3108	52.4988	O-H Stretching

C. UV spectral analysis

The UV-VIS spectrum of 4-Carboxyaniline, 4-Carboxyanilinium Nitrate and 4-Carboxyanilinium chloride is shown in fig. 5. The theoretical excitation energies, absorption wavelength and oscillator strength are noted in Table IV. These transitions are based on the contribution of molecular orbitals.

The 4-Carboxyaniline absorbs the maximum wavelength at 263.93nm and 275.84nm. It has 100% transmittance in the entire visible region which makes usefulness of the material in optical application. Energy gap of 4-Carboxyaniline is obtained theoretically by DFT method is 4.7 eV. The theoretically calculated UV spectrum of 4-Carboxyaniline is plotted in the Fig.7 which matches well with the experimental spectra [5]. A good understanding of chemical reactivity can be obtained by the electronic absorption that corresponds to the transition from the ground to the first excited state and it is mainly described by one electron excitation from the highest occupied molecular orbital to the lowest unoccupied molecular orbital [14,15]. The energy gap of the molecule was determined at B3LYP, which gives the chemical reactivity of the molecule and proves the transition within the molecule. The HOMO lying at -5.95 eV is delocalized π orbital whereas the LUMO lying at -1.37 eV is a π^* orbital, delocalized over the entire molecule with large anti-bonding character.

Optical transmission range and the cutoff wavelength are very useful factor for optical application. The energy gap of the 4-Carboxyanilinium Nitrate corresponding to the cutoff wavelength 633.44 nm and 561.27 nm is 1.96 eV and 2.21 eV respectively. When the band gap is small, the compound will be easily excited. The energy gap between HOMO and LUMO tells about the eventual charge transfer interactions taking place within the compound. The calculated HOMO and LUMO energy is -6.0 eV and -3.3 eV.

The observed electronic transition of high oscillatory strength of 4-Carboxyanilinium chloride is presented in Table 13. The 4-Carboxyanilinium chloride absorbs the maximum wavelength at 1046nm. The calculated energies of HOMO and LUMO of 4-Carboxyanilinium chloride are -4.39 eV and -3.08 eV respectively. The energy gap is found to be 1.31 eV.

Table IV
The theoretical excitation energies, absorption wavelength and oscillator strength

λmax (nm)	**Band gap (eV)**	**Energy (cm^{-1})**	**f**
4-Carboxyaniline			
263.93	4.70	37888.96	0.0374
275.84	4.49	36252.45	0.4371

4-Carboxyanilinium Nitrate			
633.44	1.96	15786.79	0.0012
561.27	2.21	17816.91	0.0053
4-Carboxyanilinium chloride			
1046	1.19	9552.89	0.078

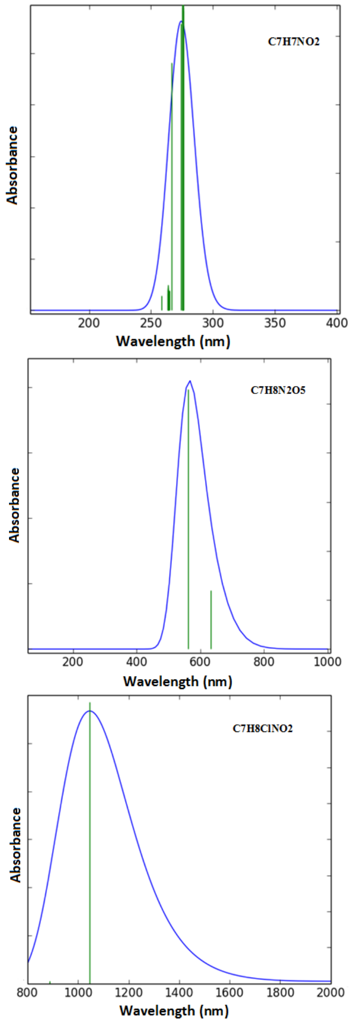


Fig 5: The UV-VIS spectrum of 4-Carboxyaniline, 4-Carboxyanilinium Nitrate and 4-Carboxyanilinium chloride

D. NMR spectral analysis

In NMR spectroscopy, the chemical shift represents the resonant frequency of a nucleus relative to a standard in a magnetic field. Often the position and number of chemical shifts are helpful to analyse the structure of a molecule. NMR chemical shifts calculations of 4-Carboxyaniline, 4-Carboxyanilinium Nitrate and 4-Carboxyanilinium chloride have been carried out by using B3LYP/6-311G GIAO (Gauge Including Atomic Orbital) method.

The chemical shifts of alkene carbon atoms in positions 2, 3, 4, 5 and 6 for 4-Carboxyaniline is higher than chemical shifts of carbonyl carbon in position 14. Enamine is the species that has an amino moiety bonded to a doubly bonded carbon atom. The chemical shift value of enamine nitrogen in position 11 is 208.4 ppm. The amine hydrogen in position 12 and 13 has the same value of 33 ppm. The oxygen atom in carbonyl (O15) group has the negative value of 147.09 and carboxyl (O16) group is 111.05. The carboxyl hydrogen atom in position 17 shows the large chemical shift value.

The oxygen (O13) in 4-Carboxyanilinium Nitrate has positive value of 86.97ppm. But oxygen (O13) in 4-Carboxyanilinium chloride has the negative value of -187.52ppm. The chemical shift value of H14 in 4-Carboxyanilinium Nitrate shows the large value as compared to hydrogen atom (H14) in 4-Carboxyanilinium chloride. In 4-Carboxyanilinium Nitrate, the observed chemical shift of N15 and N19 nuclei was identified at -384.35 ppm and 198.38 ppm respectively. In 4-Carboxyanilinium chloride, the positive chemical shift value of 213.4 ppm does exist for N15 nuclei. The peak appeared in 150.74 ppm clearly indicates the presence of Cl 19 nuclei.

E. Chemical Reactivity Studies

The frontier orbitals, HOMO and LUMO determine the molecule interacts with other species. The frontier orbital analysis helps to characterize the chemical reactivity and kinetic stability of the molecule. The 3D plots of the HOMO, LUMO are shown in fig. 6. DFT calculated HOMO, LUMO, energy gap for compounds 4-Carboxyaniline, 4-Carboxyanilinium Nitrate and 4-Carboxyanilinium chloride are presented in Table V.

The energy gap of 4-Carboxyaniline is 4.7 eV. Ionization energy describes a fundamental descriptor of the chemical reactivity of atoms and molecules. High ionization energy shows that high stability and chemical inertness and vice versa [16]. The ionization energy (I) and electron affinity (A) can be expressed through HOMO and LUMO orbital energies as $I = -E_{HOMO} = 5.95$ eV and $A = -E_{LUMO} = 1.37$ eV. The global hardness (η) is predicted by the relation $\eta = (I-A)/2 = 2.29$ eV. The electron affinity can be used in combination with ionization energy to give electronic chemical potential $\mu = -(E_{HOMO} + E_{LUMO})/2 = 3.66$ eV. If molecule has large HOMO-LUMO gap, it is a hard molecule. For small HOMO-LUMO gap, it is a soft molecule. The global electrophilicity index (ω) is calculated in terms of chemical potential and the hardness as $\omega = -(\mu^2/2\eta) = -2.924$ eV and assess the lowering of energy due to maximal electron flow between donor and acceptor. The inverse of the hardness is expressed as the global softness $S=(1/\eta) = 0.436$. $\Delta N_{max} = -\mu/\eta = -1.598$ is the maximum amount of electronic charge that the electrophile system may accept.

In the 4-Carboxyanilinium Nitrate compound, the HOMO and LUMO energies are -6.0 eV and -3.3 eV respectively. The energy gap of the molecule is 2.7 eV. The ionization energy (I) and electron affinity (A) are $I = -E_{HOMO} = 6.0$ eV and $A = -E_{LUMO} = 3.3$ eV. Absolute hardness and softness are used to identify the molecular stability and reactivity. The global hardness (η) is $\eta = (I-A)/2 = 1.35$ eV. The electronic chemical potential is found to be $\mu = -4.65$ eV. The global electrophilicity index (ω) is -8.0eV. The global softness is calculated using the relation $S=(1/\eta) = 0.740$. The maximum amount of electronic charge ΔN_{max} is -3.444.

In the 4-Carboxyanilinium Chloride compound, the HOMO and LUMO energies are -4.39 eV and -3.08 eV respectively. The energy gap of the compound is 1.31 eV. The ionization energy (I) and electron affinity (A) are $I = -E_{HOMO} = 4.39$ eV and $A = -E_{LUMO} = 3.08$ eV. The global hardness (η) is $\eta = (I-A)/2 = 0.65$ eV. The electronic chemical potential is found to be $\mu = -3.735$ eV. The global electrophilicity index (ω) is -10.73 eV. The global softness is $S=(1/\eta) = 1.538$. The maximum amount of electronic charge ΔN_{max} is -5.746.

Table V

DFT calculated HOMO, LUMO, energy gap for compounds 4-Carboxyaniline, 4-Carboxyanilinium Nitrate and 4-Carboxyanilinium chloride

Compounds	**Energy (eV)**		
	HOMO	**LUMO**	**ΔE (eV)**
C7H7NO2	-5.95	-1.37	4.7
C7H8N2O5	-6.0	-3.3	2.7
C7H8ClNO2	-4.39	-3.08	1.31

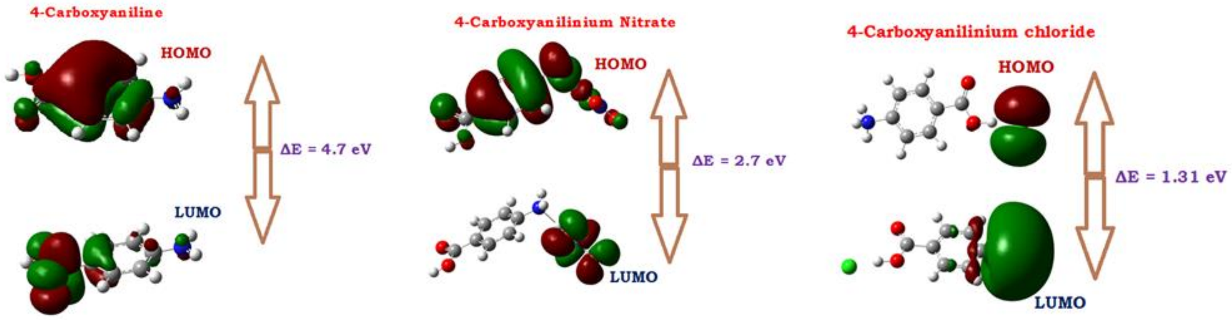


Fig 6: Molecular orbital surfaces and energies of HOMO and LUMO

F. Analysis of molecular electrostatic potential (MEP) surface

The molecular electrostatic potential represents the net electrostatic effect of a molecule which is generated from the total charge distribution in the molecule. The ESP is an important factor through which we can confirm the electrostatic potential region distribution of size and shape of molecules as well as the total physiology of the molecules [17]. Total electron density mapped with molecular electrostatic potential surface and electrostatic potential contour plots of three compounds are shown in figure 7 and 8. In the study of chemical reactivity, the region of the molecule susceptible to electrophilic or nucleophilic attack can be verified by the total electron density surface mapped with the electrostatic potential. The MESP contour map of title compounds are calculated at the B3LYP/6-311G. The different values of the electrostatic potential at the surface are mentioned by different colours. In GaussView, Potential increases in the order red < orange < yellow < green < blue. The colour code in the map varies between -6.797 a.u. (deepest red) and 6.797 a.u. (deepest blue) in compound. The red (negative) and blue (positive) colour regions in the electrostatic potential surface represent the regions susceptible to the attack of electrophiles and nucleophiles, respectively. However, the green indicates a region with zero electrostatic potential.

In the case of 4-Carboxyaniline, the map reveals that the most possible sites for nucleophilic attack are H12 and H17 and electrophilic attack are O15 and O16. According to these obtained results, we can say that the H atoms indicate the strongest attraction and O atoms indicate the strongest repulsion. 4-Carboxyanilinium Nitrate having the positive potential are over the hydrogen atoms H14, H20, H21, H22. Also the regions of positive potential are associated with O16 and 19N. MEP map of 4-Carboxyanilinium chloride presents the strongest attraction in the following atoms H16, H17, H18 and 15N.

In 4-Carboxyanilinium chloride, there is no closed contour observed in the map around nitrogen mentioning a nucleophilic substitution reaction can occur at the site.

G. Dipole moment

DFT calculated dipole moment components (μ_x, μ_y, μ_z), modulus (μ) for the title compounds are tabulated in Table VI. The dipole moment (μ) is one of the important electronic parameter that results from non-uniform distribution of charges on the various atoms in the molecule. Dipole moment for three compounds has been calculated along the three Cartesian directions. In the case of 4-Carboxyanilinium chloride, Dipole moment along the molecular X-axis is much larger than the dipole moment component along the transverse axes. Amongst the three compounds, 4-Carboxyanilinium chloride has large dipole moment than the 4-Carboxyaniline and 4-Carboxyanilinium Nitrate.

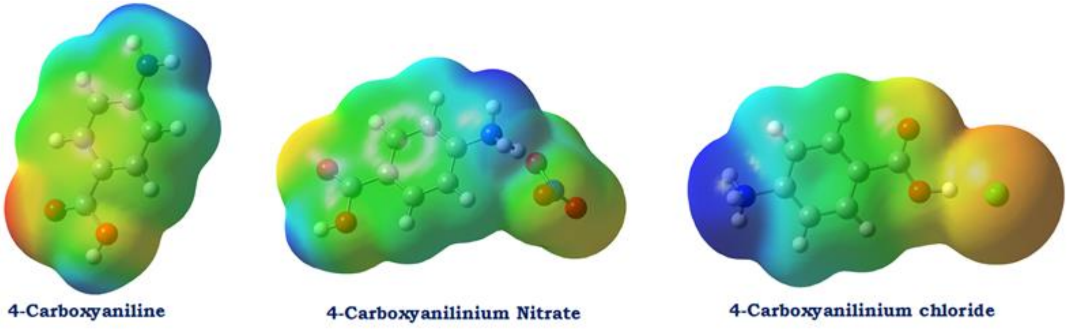


Fig 7: Total electron density mapped with molecular electrostatic potential surface

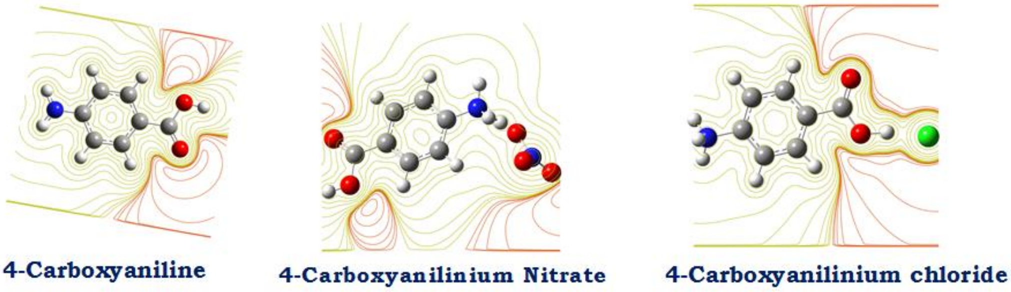


Fig 8: 2D Contour plot of 4-Carboxyaniline, 4-Carboxyanilinium Nitrate and 4-Carboxyanilinium chloride

Table VI

DFT calculated dipole moment components (μ_x, μ_y, μ_z), modulus (μ) for compounds 4-Carboxyaniline, 4-Carboxyanilinium Nitrate and 4-Carboxyanilinium chloride

Compounds	Dipole moment (μ in Debye)			
	μ_x	μ_y	μ_z	μ_{total}
C7H7NO2	0.8839	-3.4113	0.0000	3.5240
C7H8N2O5	-7.3490	6.3078	-3.0747	10.1612
C7H8ClNO2	-21.5227	0.8042	-0.6638	21.5479

Table VII

Polarizability components, isotropic component, polarizability anisotropy and asymmetry parameter relative to the molecular polarizability tensor α in the Cartesian reference frame for compounds 4-Carboxyaniline and 4-Carboxyanilinium chloride

Compounds	α_{xx}	α_{yy}	α_{zz}	α^{iso}	$\Delta\alpha$	η_α
C7H7NO2	146.117	90.668	34.898	90.561	83.342	1.031
C7H8ClNO2	164.786	98.532	41.246	101.521	94.897	0.819

H. Polarizability

Polarizability states that the measure of distortion of a molecule in an electric field. Electrostatic intermolecular interaction energy is related to polarizability, in particular for systems without a permanent dipole moment [17]. This property measures the strength of molecular interactions, the cross sections of different scattering and collision processes, and the optical properties of a system. Polarizability components, isotropic component, polarizability anisotropy and asymmetry parameter relative to the molecular polarizability tensor α in the Cartesian reference frame for compounds 4-Carboxyaniline and 4-Carboxyanilinium chloride are presented in Table VII.

We can get the value of polarizability tensors (α_{xx}, α_{xy}, α_{yy}, α_{xz}, α_{yz}, α_{zz}) from frequency job output file of Gaussian. The asymmetry parameter (η) is given by $\eta = [(\alpha_{yy} - \alpha_{zz})/(\alpha_{xx} - \alpha^{iso})]$ where $\alpha_{xx}, \alpha_{yy}\ and\ \alpha_{zz}$ are the principle components of the molecular polarizability tensor. α^{iso} is the isotropic molecular polarizability with $\alpha^{iso} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$. Polarizability anisotropy is calculated by using the relation $\Delta\alpha = [\alpha_{xx} - (\alpha_{yy} + \alpha_{zz})/2]$. All polarizability components and the anisotropy parameter are expressed in Bohr^3 (1 Bohr =0.53Å). The asymmetry parameters for 4-Carboxyaniline and 4-Carboxyanilinium chloride are 1.031 and 0.819 respectively.

I. Thermodynamic properties

The total energy of a molecular system is equal to the sum of translational, rotational, vibrational and electronic energies. The molecular partition function represents the product of the translational, rotational, and electronic partition functions of the molecule [18]. The thermochemical analysis is found at room temperature of 298.15 K and 1 atmospheric pressure. The calculated thermodynamic parameters are presented in Table VIII. The total energies actually decrease with the increase of the basis set dimension. The zero point vibrational energy of 4-Carboxyanilinium nitrate is high as compared to the other two compounds. From the table we can conclude that total thermal energy of compound increases when the entropy of the system increases.

Table VIII
The calculated thermodynamic parameter of 4-Carboxyaniline, 4-Carboxyanilinium Nitrate and 4-Carboxyanilinium chloride employing B3LYP/6-311G method

Thermodynamic parameters (298K)	C7H7NO2	C7H8N2O5	C7H8ClNO2
SCF energy (a.u)	-476.17023	-757.04669	-936.92293
Total energy (thermal), Etotal (kcal mol^{-1})	88.322	108.107	96.325
Heat capacity at const. volume, Cv (cal mol^{-1} K^{-1})	33.249	47.387	36.170
Entropy, *S* (cal mol^{-1} K^{-1})	90.259	120.837	104.031
Vibrational energy, Evib (kcal mol^{-1})	86.544	106.330	94.547
Zero-point vibrational energy, E0 (kcal mol^{-1})	82.97954	99.79747	89.95420
Rotational constants (GHz)			
A	3.7481379	1.54383	2.95593
B	0.7640616	0.25371	0.32867
C	0.6346812	0.23597	0.29626

IV. Results and Discussion

We have used the B3LYP functional with the standard basis set 6-311G due to its successful application for larger organic compounds as well as hydrogen bond systems in past. Comparison of the calculated and experimental frequencies suggests the important information about the ability of the computational method to describe the vibrational modes. The difference between the observed and scaled frequencies of the fundamentals is very small. The presence of functional groups and elements were verified using IR and Raman spectrum. The optical properties of three compounds were analysed by UV-Visible spectrum and also the optical band gap of these compounds are determined. The 4-Carboxyaniline crystal structure indicates that twinning and disorder are common. In this case, the carboxyl and amino groups are slightly interchanged from the plane of benzene rings and the nitrogen atoms are non-planar. In 4-Carboxyanilinium Chloride, the amine group is protonated and the values of the corresponding C-N bond lengths are 1.471Å and 1.464Å. The 4-Carboxyaniline absorbs the maximum wavelength at 263.93nm and 275.84nm. It has 100% transmittance in the entire visible region which makes usefulness of the material in optical application.

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