

Density Functional Theory and Abinitio Studies of Vibrational Spectra of Nalidixic Acid

S. Muthu

Department of Physics, Sri Venkateswara College of Engg.
Sriperumbudur – 602105, Tamil nadu
E-mail: muthu@svce.ac.in

E. Elamurugu Porchelvi

Department of Physics, Kanchi Pallavan Engineering College
Kanchipuram-631502 Tamil nadu

Yusuf Erdogan

Department of Physics, Arts and Science Faculty
Ahi Evran University, Turkey-40100

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Abstract: The FTIR and FTR spectrum of Nalidixic acid has been recorded in the region of $4000\text{--}400\text{ cm}^{-1}$ and $3500\text{--}250\text{ cm}^{-1}$, respectively. The optimized geometry, frequency and intensity of the vibrational bands of Nalidixic acid were obtained by ab initio and DFT levels of theory with complete relaxation in the potential energy surface using 6-31G(d,p) basis set. A Complete vibrational assignment aided by the theoretical harmonic frequency analysis has been proposed. The harmonic vibrational frequencies calculated have been compared with experimental FTIR and FT Raman spectra. The observed and the calculated frequencies are found to be in good agreement. The experimental spectra also coincide satisfactorily with those of theretically constructed bar type spectrograms.

Keywords: FTIR and FT Raman spectra; Ab initio and DFT; Nalidixic acid; Vibrational analysis.

1. Introduction

Nalidixic acid pronounced as nal-i-Dix-ik-As-id. It is an anti-infective/antibacterial drug belonging to a Quinolone group of antibiotics. It is used in the treatment of urinary tract infection and shigellosis. Nalidixic acid is 1-ethyl-1,4-dihydro-7-methyl-4-oxo-1,8-naphthyridine-3-carboxylic acid. Its molecular formula $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3$. It is a pale yellow crystalline substance and a very weak organic acid. It is freely soluble in dichloro methane and dilute solution of alkali hydroxide¹⁻². Several investigations on the title

compound have been carried out by many researchers ³⁻⁵. They have been several investigations on the IR & Raman spectra of Nalidixic acid and its derivatives, which lead to tentative assignments on the basis of qualitative considerations. Gunasekaran et al ⁶ investigated the vibrational spectra & normal coordinate analysis on Nalidixic acid.

In the present investigation DFT is used to study the complete vibrational spectra of the title compound and to identify the various normal modes with greater wave number accuracy. Ab initio, HF and DFT calculation have been performed to support our wave number assignments. The theoretically predicted IR and Raman intensities are well in agreement with that of experimental spectral data.

2. Experimental Details

High-grade pure sample of nalidixic acid was procured from a reputed pharmaceutical company, Himedia Chemicals, India and was used without further purification. FTIR spectrum has been recorded in the region of 4000-400 cm^{-1} in the solid state and the FT Raman spectrum in the region 3500-250 cm^{-1} by using BRUKER IFS 66V spectrophotometer at SAIF, IIT Chennai India. The FTIR and FTR spectra of nalidixic acid are presented in the Fig 1 and 2.

3. Computational details

The entire calculations conducted in the present work were performed at Hartree-Fock (HF) and B3LYP levels included in the Gaussian 03W package program together with 6-31G basis set function of the density functional theory (DFT) utilizing gradient geometry optimization ⁷. The geometries were first determined at the Hartree Fock level of theory employing 6-31G(d,p) basis sets. All the geometries were then optimized using 6-31G(d,p) basis set using density functional theory (DFT) ⁸ employing the Becke's three-parameter hybrid functional ⁹ combined with Lee-Yang-Parr correlation ¹⁰ functional (B3LYP) method. The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of nalidixic acid were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. Finally calculated normal mode vibrational frequencies, provide thermodynamic properties by way of statistical mechanics. Zero point vibrational energy was also calculated in the present work. By combining the results of the Gaussview program ¹¹ with summery considerations,

vibrational frequency assignments were made with high degree of accuracy. There is always some ambiguity in defining internal coordination. However, the defined coordinate form complete set and matches quite well with the motions observed using the Gaussview programme.

4. Results and Discussion

Molecular Geometry

The optimized structure parameters of Nalidixic acid calculated by ab initio HF & DFT- B3LYP levels with the 6-31G(d,p) basis set are listed in table 1 in accordance with the atom numbering scheme is given in fig 3. Table 1 compares the calculated bond lengths and angles for Nalidixic acid with the experimentally available from X-ray data for Nalidixic acid ¹². For example, the optimized bond length of C-H in nalidixic acid fall in the range 1.1130 Å⁰-1.100 Å⁰ from B3LYP/6-31G(d,p) method are good agreement with experimental ones.

Vibrational assignments

C – C Vibrations

The ring carbon-carbon stretching vibrations ¹³ occur in the region 1625 – 1430 cm⁻¹. Neville & Shurvell ¹⁴ have identified the IR bands at 1470, 1484, 1561, 1517 cm⁻¹ in diazepam and closely related compound of benzodiazepines due to aromatic cc stretching vibrations. Based on these factors, In this present work the bands observed at 1616, 156, 1538, 1518 cm⁻¹ in FTIR and 1600, 1560, 1540, 1500 cm⁻¹ in Raman are assigned to c-c stretching vibrational modes.

O – H Vibrations

The O-H group gives rise to three vibrations namely stretching, in plane & out of plane bending vibrations. The O-H group vibrations are likely to be the most sensitive to the environment, So they pronounced shift in the spectra at the hydrogen bonded species. The hydroxyl stretching vibrations are generally ¹⁵ observed in the region around 3500 cm⁻¹. In the present study the band observed in FTIR Spectrum at 3418 cm⁻¹ and in Raman at 3420 cm⁻¹.

C-H Vibrations

The hetero aromatic structure shows the presence of C-H Stretching vibrations in the region 3100-2800 cm⁻¹, which is the characteristics region for ready identification of C-H stretching vibrations. ¹⁶ In this region band are not affected appreciably by the nature of substituents. Gunasekaran et al

¹⁷ identified the presence of C-H Stretching Vibrations in the region 2990-2820 cm^{-1} . In the present work the bands observed at 3100, 3080, 3045, 3019, 2984, 2972, 2940, 2919, 2900, 2875, and 2845 cm^{-1} in FTIR Spectrum and the band observed at 3090, 3080, 3030, 3000, 2980, 2975, 2945, 2915, 2890, 2870, and 2850 cm^{-1} in FT Raman are assigned to C-H Stretching.

N-C-H vibrations

A number of N-C-H deformation bands occur in the regions 1500, 1450, 1290-1000 & 700-720 cm^{-1} .¹⁸ In the present work the bands observed at 1384, 1353, 1327 cm^{-1} in FTIR and the bands observed at 1390, 1345, & 1325 cm^{-1} in FTR are assigned to N-C-H deformation of Nalidixic acid

C=N & C-N Vibrations

In 2,3,4 substituted pyrazole-5- one three or four bands are observed due to C=N stretching¹⁹ in the region 1705 – 1450 cm^{-1} . Imidazoles functional group have several bands of variable intensity in the range 1600-1450 due to C=N Stretching²⁰. In the present work the band observed at 1785 cm^{-1} in FTIR & at 1780 cm^{-1} in FT Raman is assigned to C=N stretching Vibrations mode.

In C-N Stretching frequencies in the side chain are rather difficult task. Since there are problems in identifying these frequencies from other Vibrations. The C-N Stretching usually lies in the region 1200-1400 cm^{-1} . In this work the band observed at 1470, 1444 & 1420 cm^{-1} in FTIR and at 1470, 1435, & 1420 cm^{-1} in FT Raman are assigned to C-N Stretching Vibrations modes.

C-C-H bending

The C-H deformation²¹⁻²² frequencies and its derivatives are found to occur in the region 1200-1050 cm^{-1} . In the present work the bend observed at 1182, 1165, 1130, 1102, 1051, 1020, 1005 and 974 cm^{-1} in FTIR and at 1190 cm^{-1} , 1175, 1110, 1100, 1050, 1020, 1000 and 985 cm^{-1} in FT Raman are assigned to C-C-H asymmetric & symmetric bending vibrations modes

C-C-C bending

The C-C-C bending bands²³⁻²⁵ always occur around 600 cm^{-1} . In the present work bands observed at 656 & 635 cm^{-1} in FTIR spectrum and at 660, 650 cm^{-1} in FT Raman are assigned to C-C-C bending modes.

Substituted Pyrimidines have number of weak to medium absorption bands in the region 650-400 cm^{-1} which are due to the deformation of C-

$\text{N}=\text{C}$, $\text{N}-\text{C}-\text{N}$, $\text{C}-\text{N}-\text{C}$, $\text{C}-\text{N}-\text{N}$ & $\text{C}-\text{C}=\text{N}$ ²³. In the present work the bands observed at 455 cm^{-1} , 485 cm^{-1} , 400 cm^{-1} in FTIR spectrum are assigned to $\text{C}-\text{N}=\text{C}$, $\text{N}-\text{C}-\text{N}$, & $\text{C}-\text{N}-\text{C}$ bending vibrations respectively. FT Raman assigned at 440 cm^{-1} , 480 cm^{-1} .

C=O Vibrations

The band due to $\text{C}=\text{O}$ Stretching Vibrations is observed in the region $1850\text{--}1550\text{ cm}^{-1}$ due to tautomerism, pyrimidines substituted with hydroxyl groups are generally in the keto form and therefore, have a strong band due to carbonyl group.²⁶⁻²⁷ In the present work, the bands observed at 1713 & 1680 cm^{-1} in FTIR Spectrum and 1720 cm^{-1} , 1690 cm^{-1} in Raman are assigned to $\text{C}=\text{O}$ Stretching mode of Vibrations, respectively.

Other molecular properties

On the basis of vibrational analysis at B3LYP/6-31G (d,p) and HF/6-31G(d,p) levels and several thermodynamic parameters are calculated and are presented in Table 5. The zero point vibration energies (ZPVE) and the entropy, $S_{\text{vib}}(T)$ are calculated to the extent of accuracy and the vibrations in ZPVEs seem to be insignificant. The total energies and the change in the total entropy of Nalidixic acid at room temperature at different methods are only marginal.

5. Conclusion

Attempts have been made in the present work for the proper frequency assignments for the compound Nalidixic acid from the FTIR and FT Raman spectra. The equilibrium geometries and harmonic frequencies of Nalidixic acid were determined and analyzed both at HF and DFT levels of theories utilizing 6-31G(d,p) basis set, giving allowance for the lone pairs through diffuse function. The difference between observed and calculated wave number values of the most of the fundamental modes is very small. Any discrepancy noted between the observed and calculated frequencies may be due to the fact that the calculations have been actually done on a single molecule in the gaseous state contrary to the experimental values recorded in presence of intermolecular interaction. Therefore, the assignment made at higher levels of theory with only reasonable deviations from the experimental values seems to be correct.

Table1. Optimized parameters for Nalidixic acid B3LYP and HF with 6-31G(d,p)

Parameters	Experi mental *	B3LYP/6- 31G(d,p)	HF /6- 31G(d,p)
Bond length			
C(17)-H(29)	1.1130	1.113	1.113
C(17)-H(28)	1.1130	1.113	1.113
C(17)-H(27)	1.1130	1.113	1.113
C(16)-H(26)	1.1130	1.113	1.113
C(16)-H(25)	1.1130	1.113	1.113
C(15)-H(24)	1.1130	1.113	1.113
C(15)-H(23)	1.1130	1.113	1.113
C(15)-H(22)	1.1130	1.113	1.113
O(13)-H(21)	0.9720	0.972	0.972
C(7)-H(20)	1.1000	1.100	1.100
C(6)-H(19)	1.1000	1.100	1.100
C(2)-H(18)	1.1000	1.100	1.100
N(1)-C(16)	1.4700	1.470	1.470
C(16)-C(17)	1.5230	1.523	1.523
C(8)-C(15)	1.4970	1.497	1.497
C(4)-O(14)	1.2080	1.208	1.208
C(3)-C(11)	1.3510	1.351	1.351
C(11)-O(13)	1.3380	1.338	1.338
C(11)-O(12)	1.2080	1.208	1.208
C(5)-C(10)	1.3370	1.337	1.337
N(1)-C(10)	1.2660	1.266	1.266
N(9)-C(10)	1.2600	1.260	1.260
C(8)-N(9)	102600	1.260	1.260
C(7)-C(8)	1.3906	1.390	1.391
C(6)-C(7)	1.3370	1.337	1.337
C(5)-C(6)	1.3370	1.337	1.337
C(4)-C(5)	1.3510	1.351	1.351
C(3)-C(4)	1.3510	1.351	1.351
C(2)-C(3)	1.3415	1.341	1.342
N(1)-C(2)	1.2660	1.266	1.266
Bond Angle			
H(29)-C(17)-(28)	109.5200	109.5	109.5
H(29)-C(17)-(27)	109.4618	109.5	109.5
H(29)-C(17)-(16)	109.4618	109.5	109.5
H(28)-C(17)-(27)	109.4418	109.5	109.4
H(28)-C(17)-(16)	109.4418	109.4	109.4
H(27)-C(17)-(16)	109.5000	109.5	109.5
H(26)-C(16)-(25)	109.5200	109.5	109.5
H(26)-C(16)-N(1)	109.4618	109.5	109.5
H(26)-C(16)-(17)	109.4618	109.5	109.5
H(25)-C(16)-N(1)	109.4418	109.4	109.4
H(25)-C(16)-C(17)	109.4418	109.4	109.4

N(1)-C(16)-C(17)	109.5000	109.5	109.5
H(24)-C(15)-H(23)	109.5200	109.5	109.5
H(24)-C(15)-H(22)	109.4618	109.5	109.5
H(24)-C(15)-C(8)	109.4618	109.5	109.5
H(23)-C(15)-H(22)	109.4418	109.4	109.4
H(23)-C(15)-C(8)	109.4418	109.4	109.4
H(22)-C(15)-C(8)	109.5000	109.5	109.5
H(21)-O(13)-C(11)	120.0000	120.0	120.0
C(3)-C(11)-O(13)	120.0000	120.0	120.0
C(3)-C(11)-O(12)	120.0000	120.0	120.0
O(13)-C(11)-O(12)	120.0000	120.0	120.0
C(5)-C(10)-N(1)	120.0000	120.0	120.0
C(5)-C(10)-N(9)	119.9988	120.0	120.0
N(1)-C(10)-N(9)	119.9988	120.0	120.0
C(10)-N(9)-C(8)	115.0000	115.0	115.0
C(15)-C(8)-N(9)	118.3320	118.3	118.3
C(15)-C(8)-C(7)	118.3320	118.3	118.3
N(9)-C(8)-C(7)	123.3361	123.3	123.3
H(20)-C(7)-C(8)	124.6135	124.6	124.6
H(20)-C(7)-C(6)	124.6135	124.6	124.6
C(8)-C(7)-C(6)	110.7730	110.8	110.0
H(19)-C(6)-C(7)	120.0000	120.0	120.0
H(19)-C(6)-C(5)	120.0000	120.0	120.0
C(7)-C(6)-C(5)	120.0000	120.0	120.0
C(10)-C(5)-C(6)	119.9987	120.0	120.0
C(10)-C(5)-C(4)	117.6000	117.6	117.6
C(6)-C(5)-C(4)	122.3986	122.4	122.4
O(14)-C(4)-C(5)	122.5000	122.5	122.5
O(14)-C(4)-C(3)	122.5000	122.5	122.5
C(5)-C(4)-C(3)	115.0000	115.0	115.0
C(11)-C(3)-C(4)	120.8848	120.9	120.9
C(11)-C(3)-C(2)	120.8848	120.9	120.9
C(4)-C(3)-C(2)	118.2304	118.2	118.2
H(18)-C(2)-C(3)	121.5992	121.6	121.6
H(18)-C(2)-N(1)	121.5992	121.6	121.6
C(3)-C(2)-N(1)	116.8016	116.8	116.8
C(16)-N(1)-C(10)	118.0000	118.0	118.0
C(16)-N(1)-C(2)	118.0000	118.0	118.0
C(10)-N(1)-C(2)	124.0000	124.0	124.0

Table 2. Vibrational wave numbers obtained for Nalidixic acid HF/6-31G(d,p)[harmonic frequency(cm^{-1}),IR intensities(Km mol^{-1}),Raman scattering activities($\text{A}^4 \text{amu}^{-1}$),Raman depolarization ratio and reduced mass(amu),force constants (m dyne A^{-1})]

Frequencies		IR Intensity		Raman Activity		Depolar (P)	Reduced masses	Force constant
Unscaled	scaled	Rel	Abs	Rel	Abs			
3790	3423	43	5	31	12	0.25	1.07	9.03
3156	2850	3	0	131	51	0.18	1.10	6.48
3139	2835	13	2	62	24	0.35	1.10	6.39
3135	2831	1	0	80	31	0.57	1.09	6.33
3013	2720	18	2	65	25	0.75	1.10	5.91
3007	2715	18	2	91	35	0.73	1.10	5.87
3002	2711	63	8	25	10	0.75	1.11	5.91
2971	2682	46	6	108	42	0.65	1.11	5.77
2966	2679	163	20	239	93	0.30	1.09	5.64
2946	2660	6	1	128	50	0.22	1.07	5.44
2945	2660	20	2	130	50	0.08	1.04	5.31
2913	2630	65	8	169	66	0.07	1.04	5.20
2130	1923	752	91	60	23	0.43	10.71	28.63
2069	1868	826	100	257	100	0.27	9.43	23.76
2019	1823	217	26	32	13	0.58	10.34	24.84
2001	1807	224	27	16	6	0.75	10.43	24.62
1963	1773	54	7	39	15	0.71	9.24	20.99
1912	1726	65	8	14	5	0.38	8.24	17.75
1875	1693	330	40	44	17	0.42	8.15	16.87
1778	1605	118	14	2	1	0.60	4.36	8.13
1728	1560	61	7	13	5	0.70	1.60	2.81
1723	1556	36	4	6	2	0.71	2.08	3.63
1710	1544	101	12	24	9	0.42	1.30	2.24
1669	1507	29	3	20	8	0.55	1.16	1.90
1653	1492	18	2	38	15	0.19	2.75	4.43
1640	1481	7	1	7	3	0.72	1.13	1.80
1636	1477	15	2	16	6	0.49	1.32	2.08
1626	1468	20	2	18	7	0.73	1.12	1.74
1591	1436	22	3	4	2	0.37	2.81	4.19
1578	1425	13	2	9	4	0.63	1.43	2.10
1574	1421	36	4	22	9	0.17	2.26	3.29
1543	1393	24	3	10	4	0.72	1.40	1.96
1490	1346	244	30	6	2	0.27	1.78	2.33
1465	1323	2	0	8	3	0.75	1.11	1.41
1451	1310	373	45	4	1	0.71	1.70	2.11
1394	1259	15	2	1	0	0.28	2.07	2.37
1338	1208	4	0	2	1	0.74	1.36	1.44
1311	1184	15	2	1	1	0.31	1.58	1.60
1297	1171	21	3	9	4	0.42	1.42	1.41
1267	1144	18	2	7	3	0.32	2.11	1.99

1235	1115	1	0	3	1	0.68	1.73	1.55
1224	1105	1	0	1	0	0.70	1.29	1.14
1207	1090	4	1	2	1	0.68	1.51	1.29
1178	1064	20	2	2	1	0.42	1.92	1.57
1131	1022	23	3	4	2	0.53	1.31	0.99
1124	1015	21	3	4	1	0.35	2.55	1.90
1087	982	27	3	10	4	0.22	2.99	2.09
1056	953	6	1	3	1	0.72	1.45	0.95
1012	914	17	2	2	1	0.61	2.89	1.74
999	902	4	0	2	1	0.68	1.23	0.73
984	888	28	3	4	2	0.48	1.30	0.74
937	846	2	0	21	8	0.07	3.83	1.98
857	774	47	6	7	3	0.75	6.92	3.00
835	754	3	0	3	1	0.14	4.38	1.80
814	735	21	2	4	1	0.59	4.64	1.81
806	728	1	0	2	1	0.49	5.27	2.02
763	689	2	0	7	3	0.12	4.04	1.39
736	665	42	5	2	1	0.17	4.75	1.52
735	664	5	1	4	2	0.15	5.18	1.65
687	621	138	17	5	2	0.32	1.43	0.40
642	580	5	1	1	0	0.75	4.80	1.17
609	550	12	1	1	1	0.61	5.60	1.22
550	497	2	0	1	1	0.65	4.07	0.73
540	488	13	2	4	1	0.07	6.85	1.18
516	466	16	2	3	1	0.69	5.69	0.89
502	453	0	0	1	0	0.73	1.11	0.16
452	408	2	0	4	2	0.54	3.83	0.46
440	397	13	2	3	1	0.63	4.39	0.50
406	367	1	0	6	2	0.29	5.44	0.53
383	346	3	0	1	0	0.65	5.97	0.52
360	325	1	0	2	1	0.73	4.60	0.35
272	245	4	1	0	0	0.57	2.53	0.11
204	185	5	1	1	1	0.72	6.75	0.17
164	148	3	0	0	0	0.20	3.87	0.06
132	119	4	0	3	1	0.57	4.59	0.05
101	91	1	0	1	0	0.61	8.40	0.05
63	57	1	0	1	0	0.69	5.20	0.01
55	50	7	1	1	0	0.75	10.12	0.11
43	39	2	0	2	1	0.72	7.62	0.09
35	31	2	0	1	0	0.45	9.29	0.19
19	17	1	0	1	0	0.67	4.29	0.24

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Frequencies		IR Intensity		Raman Activity		Depolar (P)	Reduced masses	Force constants
Unscaled	scaled	Rel	Abs	Rel	Abs			
3723	3578	10	2	65	23	0.26	1.07	8.70
3081	2961	6	1	170	61	0.19	1.10	6.17
3064	2945	1	0	78	28	0.61	1.09	6.03
3053	2934	13	2	69	25	0.33	1.10	6.03
2961	2845	11	2	63	23	0.75	1.10	5.70
2953	2838	12	2	96	34	0.72	1.10	5.66
2943	2828	45	8	32	11	0.75	1.11	5.67
2914	2800	31	6	88	32	0.71	1.11	5.55
2905	2791	154	28	278	100	0.33	1.09	5.41
2882	2770	9	2	84	30	0.40	1.06	5.21
2881	2769	12	2	201	72	0.05	1.03	5.06
2846	2735	66	12	274	99	0.12	1.04	4.95
2046	1966	474	87	59	21	0.39	11.59	28.57
1975	1898	545	100	229	82	0.21	11.64	26.75
1949	1873	121	22	32	11	0.69	10.34	23.15
1933	1858	134	25	120	43	0.41	11.37	25.03
1883	1809	23	4	58	21	0.57	9.94	20.76
1853	1780	55	10	37	13	0.24	10.15	20.53
1827	1756	41	8	25	9	0.38	9.83	19.34
1727	1659	132	24	17	6	0.19	8.57	15.04
1670	1605	83	15	3	1	0.61	9.68	15.91
1641	1577	80	15	30	11	0.14	6.39	10.14
1578	1517	4	1	18	7	0.67	1.04	1.53

1550	1489	32	6	5	2	0.55	1.37	1.93
1531	1471	49	9	31	11	0.60	1.26	1.74
1523	1464	43	8	13	5	0.75	1.55	2.11
1512	1453	4	1	15	5	0.75	1.08	1.46
1501	1443	19	4	10	4	0.43	2.17	2.88
1491	1433	24	4	10	4	0.75	1.37	1.79
1484	1426	6	1	4	2	0.73	1.37	1.78
1437	1381	17	3	31	11	0.37	1.30	1.59
1409	1354	51	9	17	6	0.52	1.50	1.76
1397	1343	140	26	6	2	0.21	1.72	1.98
1343	1291	2	0	7	3	0.75	1.12	1.19
1304	1254	133	24	5	2	0.70	1.95	1.95
1295	1245	68	12	5	2	0.30	1.99	1.97
1218	1170	3	1	3	1	0.74	1.39	1.22
1211	1164	12	2	4	2	0.73	1.37	1.18
1175	1129	53	10	4	2	0.54	1.86	1.51
1134	1090	37	7	5	2	0.18	1.77	1.34
1129	1085	37	7	10	4	0.35	1.51	1.13
1095	1053	4	1	3	1	0.56	1.57	1.11
1082	1039	13	2	2	1	0.27	1.85	1.28
1071	1029	4	1	2	1	0.54	1.32	0.89
1049	1008	17	3	3	1	0.51	2.82	1.83
1031	991	12	2	13	5	0.13	2.24	1.40
966	929	4	1	6	2	0.41	1.91	1.05
949	912	16	3	3	1	0.68	2.21	1.17
933	896	15	3	3	1	0.61	1.31	0.67
902	867	3	1	10	3	0.15	1.39	0.67
875	841	19	4	3	1	0.75	1.27	0.57

864	831	5	1	27	10	0.09	2.00	0.88
773	743	0	0	5	2	0.13	4.14	1.46
748	719	4	1	4	2	0.44	3.72	1.23
736	707	20	4	5	2	0.72	7.29	2.33
704	676	10	2	2	1	0.64	6.44	1.88
687	660	2	0	5	2	0.19	4.68	1.30
674	648	4	1	1	0	0.27	5.07	1.36
633	608	18	3	6	2	0.26	5.46	1.29
564	542	5	1	1	0	0.70	5.50	1.03
544	523	4	1	1	0	0.68	5.46	0.95
498	479	4	1	3	1	0.20	4.04	0.59
497	478	9	2	3	1	0.30	7.24	1.05
459	441	16	3	3	1	0.68	6.87	0.85
408	392	28	5	3	1	0.54	2.56	0.25
406	390	2	0	2	1	0.75	1.58	0.15
389	373	24	4	2	1	0.74	1.92	0.17
369	355	2	0	10	3	0.26	3.79	0.30
334	321	6	1	1	0	0.71	6.87	0.45
288	277	46	9	1	0	0.59	1.74	0.09
275	264	9	2	2	1	0.49	3.24	0.14
210	201	5	1	0	0	0.31	2.41	0.06
152	146	8	1	2	1	0.63	5.99	0.08
106	102	1	0	1	0	0.08	3.50	0.02
93	90	2	0	4	1	0.54	4.28	0.02
76	73	1	0	1	0	0.55	8.45	0.06
63	60	2	0	1	0	0.50	5.03	0.05
58	56	3	1	3	1	0.69	9.26	0.14
41	39	4	1	3	1	0.48	9.74	0.23

32	31	8	1	1	1	0.40	9.36	0.30
19	19	1	0	2	1	0.49	4.40	0.26

Table 4 Experimental and computed frequencies (cm^{-1}) with assignments of Nalidixic acid B3LYP and HF with 6-31G(d,P)

IR	RAMAN	HF	B3LYP	Assignments (% PED)
3418(w)	3420(vw)	3423	3578	O-H stretching (100)
3100(w)	3090(w)	2850	2961	C-H asymmetric stretching (99)
3080(w)	3080(w)	2835	2945	C-H asymmetric stretching (100)
3045(w)	3030(vw)	2831	2934	C-H asymmetric stretching (99)
3019(w)	3000(vw)	2720	2845	C-H asymmetric stretching (95)
2984(w)	2980(vw)	2715	2838	C-H asymmetric stretching (98)
2972(w)	2975(vw)	2711	2828	C-H asymmetric stretching (94)
2940(w)	2945(vw)	2682	2800	C-H symmetric stretching (99)
2919(w)	2915(vw)	2679	2791	C-H symmetric stretching (91)
2900(w)	2890(vw)	2660	2770	C-H symmetric stretching (96)
2875(w)	2870(vw)	2660	2769	C-H symmetric stretching (95)
2845(w)	2850(vw)	2630	2735	C-H symmetric stretching (96)
1935(vw)	1930(vw)	1923	1966	C=C asymmetric stretching (96)
1875(vw)	1875(vw)	1868	1898	C=C asymmetric stretching (98)
1822(vw)	1830(vw)	1823	1873	C=C symmetric stretching (96)
1805(vw)	1800(vw)	1807	1858	C=C symmetric stretching (90)
1785(vw)	1780(vw)	1773	1809	C=N symmetric stretching (77)
1713(vs)	1720(m)	1726	1780	C=O asymmetric stretching (93)
1680(m)	1690(w)	1693	1756	C=O symmetric stretching (92)
1616(vs)	1600(vs)	1605	1659	C-C asymmetric stretching (90)
1563(m)	1560(m)	1560	1605	C-C asymmetric stretching (90)
-	1550(m)	1556	1577	C-C asymmetric stretching (91)
1538(m)	1540(w)	1544	1517	C-C symmetric (88)/HCH in plane bending (47)
1518(s)	1500(vw)	1507	1489	C-C symmetric (82)/HCH in plane bending (52)
-	1490(m)	1492	1471	C-C symmetric(82)/HCH in plane bending (63)
-	1485(m)	1481	1464	C-C symmetric (84)/HCH in plane bending (50)
1472(vs)	1475(s)	1477	1453	C-O symmetric stretching (78)
1470(vs)	1470(m)	1468	1443	C-N asymmetric stretching (86)
1444(vs)	1435(m)	1436	1433	C-N asymmetric stretching (84)
-	-	1425	1426	C-N symmetric stretching (68)
1420(s)	1420(m)	1421	1381	C-N symmetric stretching (84)
1384(s)	1390(m)	1393	1354	N-C-H asymmetric bending (53)
1353(s)	1345(s)	1346	1343	N-C-H asymmetric bending (51)
1327(s)	1325(s)	1323	1291	N-C-H symmetric bending (52)

1295(s)	1300(m)	1310	1254	CH ₃ bending (78)
1253(s)	1250(vw)	1259	1245	CH ₃ bending (80)
1228(s)	1200(vw)	1208	1170	C-O-H symmetric bending (76)
1182(m)	1190(vw)	1184	1164	C-C-H asymmetric bending (27)
1165(m)	1175(vw)	1171	1129	C-C-H asymmetric bending (30)
1130(s)	1110(vw)	1144	1090	C-C-H asymmetric bending (32)
1102(m)	1100(vw)	1115	1085	C-C-H asymmetric bending (28)
1090(m)	-	1105	1053	C-C-H asymmetric bending (34)
1070(m)	-	1090	1039	C-C-H symmetric bending (50)
1051(m)	1050(w)	1064	1029	C-C-H symmetric bending (56)
1020(m)	1020(vw)	1022	1008	C-C-H symmetric bending (48)
1005(m)	1000(vw)	1015	991	C-C-H symmetric bending (42)
974(s)	985(w)	982	929	C-C-H symmetric bending (46)
962(m)	950(vw)	953	912	C-C=N bending (52)
930(w)	-	914	896	O-C=O bending (46)
-	900(vw)	902	867	HCH bending (out of plane) (88)
875(w)	880(vw)	888	841	HCH bending (out of plane) (72)
847(vw)	850(vw)	846	831	HCH bending (out of plane) (79)
806(s)	790(s)	774	743	O=C-C bending (asymmetric) (70)
778(w)	750(m)	754	719	C-C=C asymmetric bending (62)
738(vw)	735(m)	735	707	C-C=C asymmetric bending (65)
706(w)	725(m)	728	676	C-C=C symmetric bending (60)
675(vw)	680(vw)	689	660	C-C=C symmetric bending (58)
656(w)	660(vw)	665	648	C-C-C asymmetric bending (86)
635(w)	650(vw)	664	608	C-C-C symmetric bending (82)
610(vw)	-	621	542	C=N-C bending (23)
585(vw)	600(w)	580	523	C-C=O bending (symmetric) (86)
560(vw)	550(w)	550	479	C-C-O bending (29)
513(vw)	500(w)	497	478	N-C-N bending (32)
485(w)	480(vw)	488	441	C=C-N asymmetric bending (42)
460(vw)	465(vw)	466	392	C=C-N symmetric bending (67)
455(vw)	440(w)	453	390	C-N-C bending (43)
-	-	408	373	C-C-N bending (26)
-	400(vw)	397	355	C-N-C asymmetric bending (23)
-	-	367	321	C-N-C symmetric bending (24)
-	-	346	277	C-CH ₃ in plan bending
-	-	325	264	C-CH ₃ in plan bending
-	-	245	201	CH ₃ -Twisting (84)

-	-	185	146	CH ₃ -Twisting (86)
-	-	148	102	C-CHO Out of plan bending (75)
-	-	119	90	C-CHO Out of plan bending (74)
-	-	91	73	CHO Out of plan bending (76)
-	-	57	60	CH ₃ Wagging (84)
-	-	50	56	CH ₃ Wagging (83)
-	-	39	39	CH ₃ Rocking (82)
-	-	31	31	CH ₃ Rocking (86)
-	-	17	19	CH ₃ Rocking (81)

Table 5 Theoretically computed energies (a.u), zero point ,vibrational energies (kcal mol⁻¹), dipole moment (I) and heat capacity (K cal mol⁻¹ K⁻¹).

Parameters	HF 6-31G(d,p)	B3LYP6-31G(d,p)
Zero point energy	156.14939	146.23896
Rotational constant	0.87238 0.39837 0.30365	0.87259 0.39836 0.30365
Entropy		
Total	162.592	152.847
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	160.815	151.069
Dipole moment	11.9209	13.6678

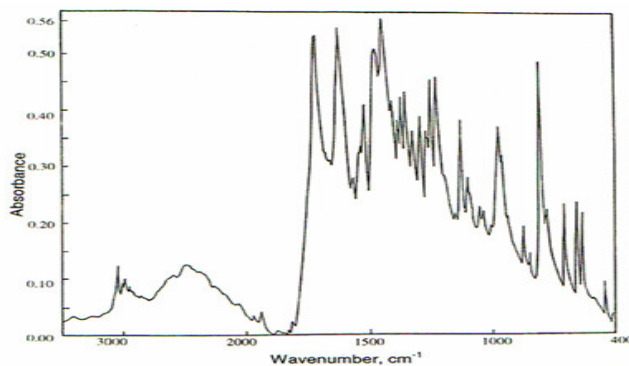


Fig.1. FTIR spectrum of Nallidixic Acid

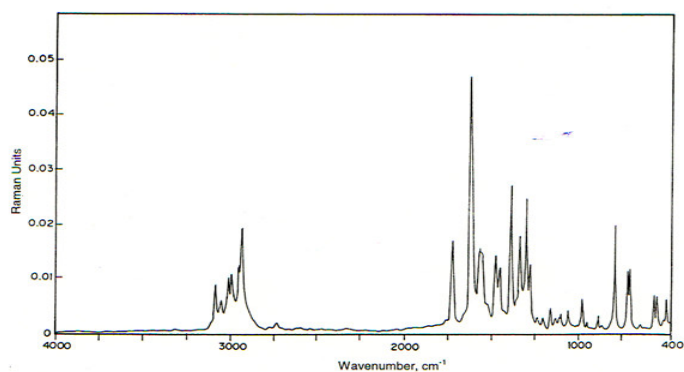


Fig.2 FT Raman spectrum of Nalidixic Acid

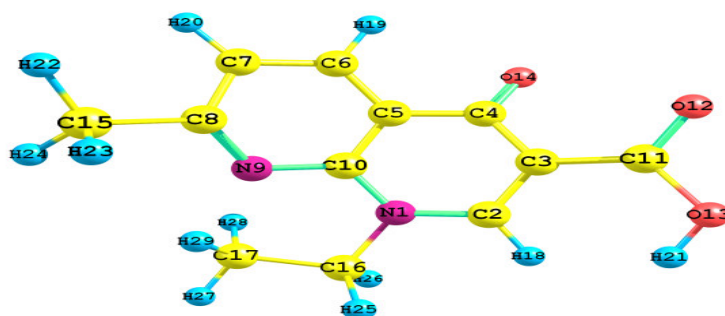


Fig 3 The atom numbering for Nalidixic acid molecule

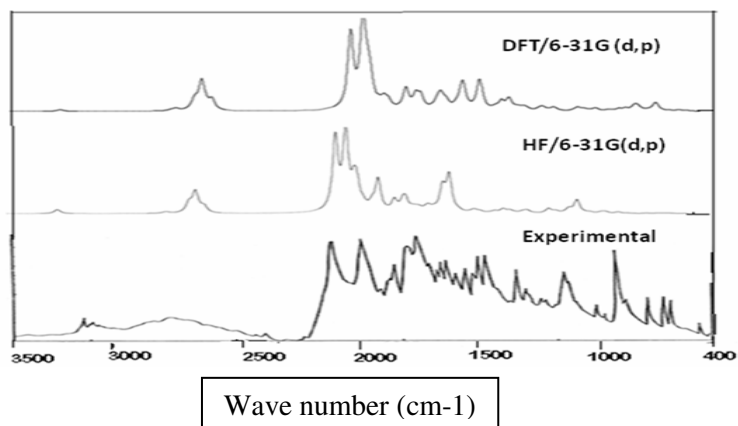


Fig.4 Comparative representation of FTIR spectra

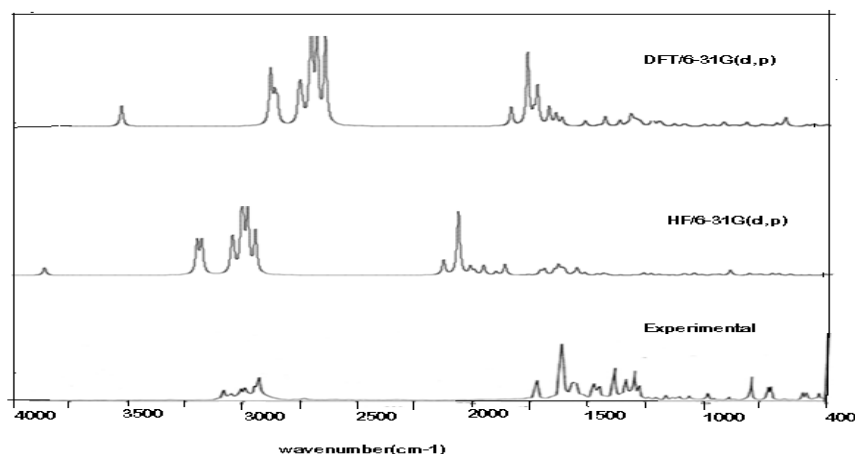


Fig. 5 Comparative Representation of FTIR Spectrum

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