

Vibrational Spectroscopic Investigations and Molecular Orbital Investigations using Ab Initio and Density Functional Theory Analysis on the Structure of 4-bromo-3-nitrobenzaldehyde

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Abstract—Benzaldehyde is best known as being artificial essential oil of almond and it has many other uses such as; the manufacturing of dyes, perfumes, flavourings, cinnamic and mandelic acids, and it is also used as a solvent. Some more recent developments in the use of benzaldehyde are for the health and agriculture industries. Due to these basic reasons there exist a vast field of study of substituted benzaldehydes. Extensive studies have been carried out on the structures and vibrational spectroscopic properties of benzaldehydes by the help of Raman and IR spectra. The optimized geometry, frequency and intensity of the vibrational bands of 4-bromo-3-nitrobenzaldehyde (4,3BNB) were obtained by the ab initio and Density Functional Theory (DFT) levels of theory with complete relaxation in the potential energy surface using different basis sets and the results thus obtained were compared with the experimental data. All the calculations were carried out by the help of Gaussian 09 program package.

Keywords: 4-bromo-3-nitrobenzaldehyde (4,3BNB), vibrational spectroscopic properties, density functional theory (DFT), ab-initio, Gaussian 09.

INTRODUCTION

Benzaldehydes and its derivatives are one of the the simplest in aromatic aldehydes and is known as artificial essential oil of almond it has many other uses such as in manufacturing of dyes, perfumes, flavorings, cinnamic and mandelic acids, and it is also used as a solvent[1]. It is synthesized in laboratories from toluene being chlorinated to benzyl chloride or by direct oxidation of toluene with manganese dioxide. Some more recent developments in the use of benzaldehyde are for the health and agriculture industries. Benzaldehyde is being used as a pesticide and also as an anticancer agent and have shown anti tumour activity in mice.[1,2] It is used as a bee repellent in the harvesting of honey. These uses are still in development but would be very helpful in solving some of these problems of today. The benzaldehyde and its derivatives have received attention because of their chemical and biological importance. The benzaldehyde and substituted benzaldehydes have been subjected to various spectroscopic studies [3-7]. In this light a vibrational spectral study and corresponding ab initio calculations are carried out for the compound 4-bromo-3-nitrobenzaldehyde(further abbreviated as 4,3BNB)

Computational

Experimental and theoretical investigations have been focused on elucidating the structure and normal vibrations of benzaldehyde and its derivatives. Ab initio Density functional theory calculations are reported to provide excellent vibrational frequencies of aromatic organic compounds. The molecular structures of benzaldehyde derivatives in the ground state were computed by Hartree-fock and density functional theory (DFT) methods with Gaussian09 program [8]. DFT method used Becke's three-parameter hybrid functional of Lee, Yang, and Parr (LYP). The following basis sets B3LYP/3-21(d, p) and B3LYP/6-311G(d, p) were used. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true energy minimum, as revealed by the absence of imaginary values in the wave number calculations.

Molecular structure

The molecular structure of the mentioned compound 4,3BNB is shown in Figure 1. The optimized bond lengths, bond angles and dihedral angles of the compound is calculated by B3LYP method using 6-311++G (d,p) basis sets are listed in Table 1 is in accordance with atom numbering scheme as shown in Fig. 1. Since the exact crystal structure of the compound BMB is not available till now, the optimized structure can only be compared with other similar system for which the crystal structures have been solved. [9]

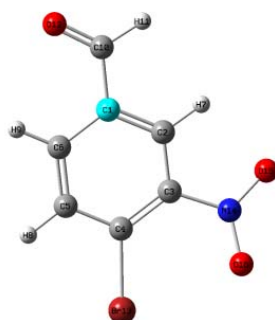


Figure 1

Table 1: Calculated Optimized Geometrical Parameters of 4,3BMB, at B3LYP/6-31G(d,p): bond length (Å), bond angle(°), dihedral angles(°)

S. No	Atoms of molecule	Bond length (Å)	Angle between atoms (°)	Bond angle (°)	Dihedral angle between atoms (°)	Dihedral angle (°)
1.	R(1,2)	1.3952	A(2,1,6)	119.9985	D(6,1,2,3)	0.0323
2.	R(1,6)	1.3948	A(2,1,10)	119.9972	D(6,1,2,7)	179.9532
3.	R(1,10)	1.54	A(6,1,10)	120.0043	D(10,1,2,3)	-179.9729
4.	R(2,3)	1.3947	A(1,2,3)	120.0086	D(10,1,2,7)	-0.052
5.	R(2,7)	1.0997	A(1,2,7)	119.9808	D(2,1,6,5)	0.0149
6.	R(3,4)	1.3954	A(3,2,7)	120.0106	D(2,1,6,9)	179.9892
7.	R(3,14)	1.47	A(2,3,4)	119.9942	D(10,1,6,5)	-179.9729
8.	R(4,5)	1.3948	A(2,3,14)	120.0128	D(10,1,6,9)	-0.0056
9.	R(4,13)	1.91	A(4,3,14)	119.993	D(2,1,10,11)	-89.9606
10.	R(5,6)	1.3951	A(3,4,5)	119.994	D(2,1,10,12)	90.0394
11.	R(5,8)	1.0998	A(3,4,13)	119.9811	D(6,1,10,11)	90.0341
12.	R(6,9)	1.0996	A(5,4,13)	120.0249	D(6,1,10,12)	-89.9659
13.	R(10,11)	1.07	A(4,5,6)	120.0047	D(1,2,3,4)	-0.0568
14.	R(10,12)	1.2584	A(4,5,8)	120.0113	D(1,2,3,14)	179.9619
15.	R(13,14)	1.36	A(6,5,8)	119.984	D(7,2,3,4)	-179.9777
16.	R(13,15)	1.36	A(1,6,5)	120.0	D(7,2,3,14)	0.041
17.			A(1,6,9)	120.008	D(2,3,4,5)	0.0341
18.			A(5,6,9)	119.992	D(2,3,4,13)	-179.9964
19.			A(1,10,11)	119.8865	D(14,3,4,5)	-179.9846
20.			A(1,10,12)	120.2269	D(14,3,4,13)	-0.0151
21.			A(11,10,12)	119.8865	D(2,3,14,15)	-59.6278
22.			A(3,14,15)	109.4712	D(2,3,14,16)	60.3722
23.			A(3,14,16)	109.4712	D(4,3,14,15)	120.3909
24.			A(15,14,16)	109.4713	D(4,3,14,16)	-119.6091
25.					D(3,4,5,6)	0.0131
26.					D(3,4,5,8)	-179.9995
27.					D(13,4,5,6)	-179.9563
28.					D(13,4,5,8)	0.0311
29.					D(4,5,6,1)	-0.0376
30.					D(4,5,6,9)	179.9881
31.					D(8,5,6,1)	179.975
32.					D(8,5,6,9)	0.0007

Vibrational spectra A detailed study of vibrational spectra is carried out, the ab initio HF and DFT calculations are performed by Gaussian 09 [8] at different basis sets and the results obtained are compared with the earlier reported values in the literature. A comparative chart of the different frequencies obtained by different calculations is displayed in table 2.

Table 2

S. No.	Hartree Fock	3-21G	6-31G
1.	49.68	18.19	34.46
2.	94.14	86.49	83.53
3.	134.09	124.10	116.17
4.	169.08	155.54	155.94
5.	199.48	194.66	181.42
6.	244.90	243.10	219.03
7.	302.39	282.11	275.60
8.	350.16	327.70	318.24
9.	357.25	329.51	321.91
10.	396.55	361.32	372.60
11.	496.16	471.19	457.62
12.	530.83	480.31	481.17
13.	614.88	568.92	551.36
14.	664.71	599.11	614.30
15.	735.09	678.33	676.75
16.	776.56	696.19	714.58
17.	787.48	724.41	733.47
18.	858.61	792.57	802.71
19.	931.92	837.62	812.06
20.	979.13	907.24	894.92
21.	1023.51	907.54	929.01
22.	1140.76	1021.79	993.09
23.	1165.64	1068.09	1046.34
24.	1200.18	1077.30	1068.88
25.	1226.06	1094.92	1073.69
26.	1239.09	1129.96	1143.24
27.	1271.35	1157.94	1191.57
28.	1301.87	1182.37	1249.52
29.	1317.55	1228.98	1276.55
30.	1356.82	1312.85	1325.03
31.	1414.44	1340.90	1376.91
32.	1451.91	1358.20	1414.85
33.	1525.99	1414.36	1450.34
34.	1571.62	1446.16	1482.38
35.	1661.55	1522.82	1534.05
36.	1730.90	1587.28	1611.76
37.	1785.06	1632.93	1654.45
38.	1911.57	1717.41	1709.84
39.	3199.67	2949.00	2994.07
40.	3394.27	3223.08	3232.89
41.	3414.84	3243.00	3243.13
42.	3420.66	3246.56	3251.27

Aldehyde Group Vibration In aldehyde group the C–H stretching vibrations usually appear in the region 2871–2806 cm^{-1} [10], in our study the DFT calculated bands at 2949.00 cm^{-1} for 3-21 and 2994.07 cm^{-1} for 6-32 basis set shows close approximation to the experimental value. The carbonyl (C=O) stretching vibrations in the substituted benzaldehydes are reported near 1700 cm^{-1} [10], the HF band at 1730.90 cm^{-1} and DFT calculated band at 1717.41 cm^{-1} for 3-21 basis set and 1709.84 cm^{-1} for 6-32 basis set can be assigned to this mode. Aldehyde group CHO deformation vibrations found in the region 975–780 cm^{-1} [11], the HF band at 787.48, 858.61, 931.92 cm^{-1} and DFT band for basis set 3-21 at 792.57, 837.62, 907.24, 907.54 cm^{-1} and for basis set 6-32 the bands at 802.71, 812.06, 894.92, 929.01 cm^{-1} can be assigned to this mode.

C-H Vibrations The aromatic structure shows C–H stretching vibration in the region 3100–3000 cm^{-1} [12] in our study the HF band at 3199.67 cm^{-1} and DFT band for basis set 3-21 at 2949.00 cm^{-1} and for basis set 6-32 2994.07 cm^{-1} can be assigned to C-H stretching. The C–H out-of-plane bending vibrations of 4,3-BNB was identified at 858.61 cm^{-1} for the HF and 837.62 cm^{-1} for DFT 3-21 basis set and 812.06 cm^{-1} for DFT 6-32 basis set are found to be well within their characteristic region and literature [13,14]

So we have seen that the values obtained by abinitio HF and DFT calculations for some prominent modes were in good agreement with the experimental reported values. The IR and Raman spectra thus obtained by the calculations are displayed in following figures. Figures 2,3 and 4

shows IR spectra for HF, DFT 3-21, and DFT 6-32 basis sets respectively, and similarly figures 5,6 and 7 shows Raman spectra for HF, DFT 3-21, and DFT 6-32 basis sets respectively.

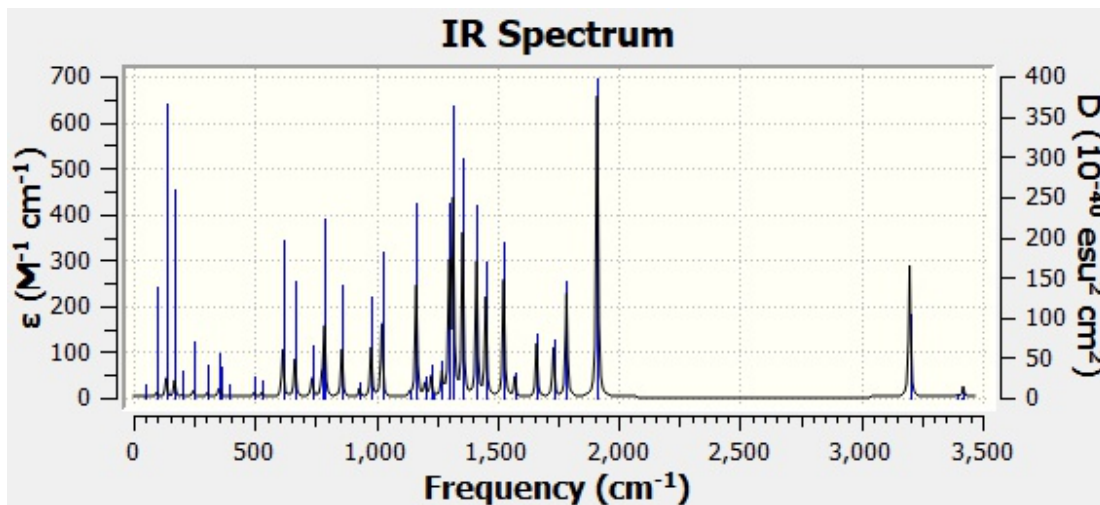


Figure 2

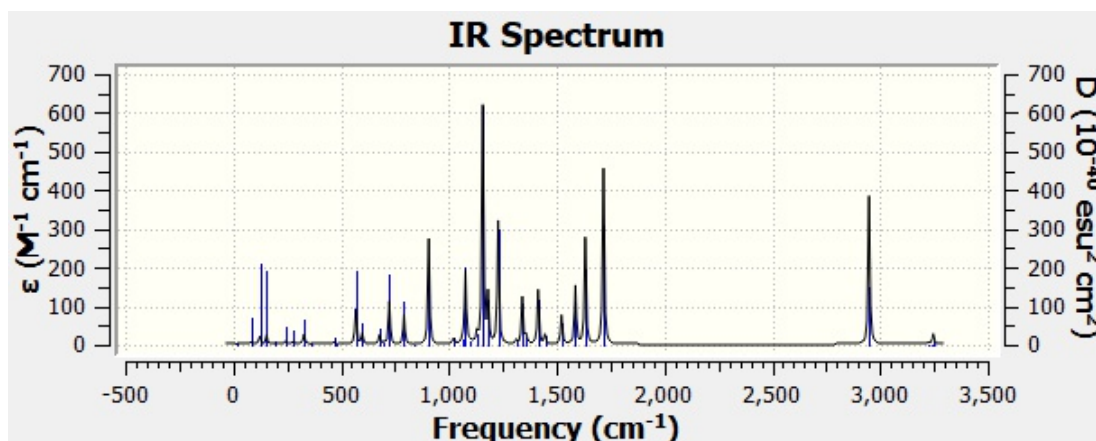


Figure 3

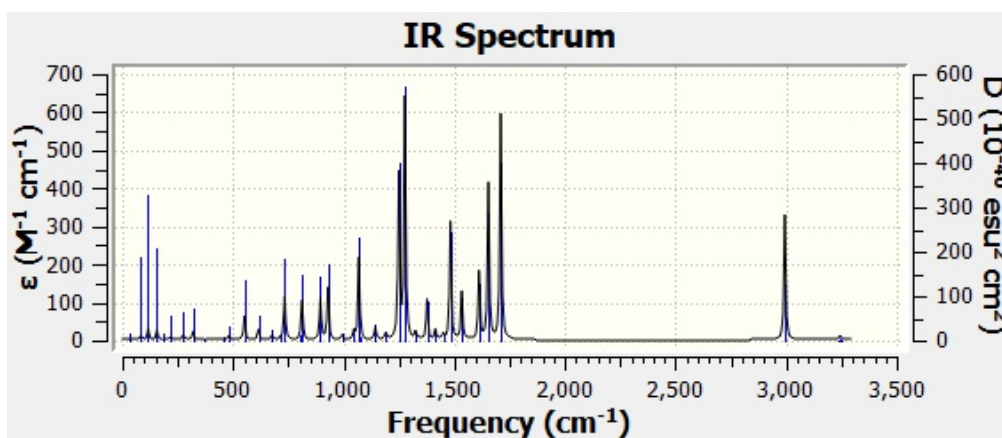


Figure 4

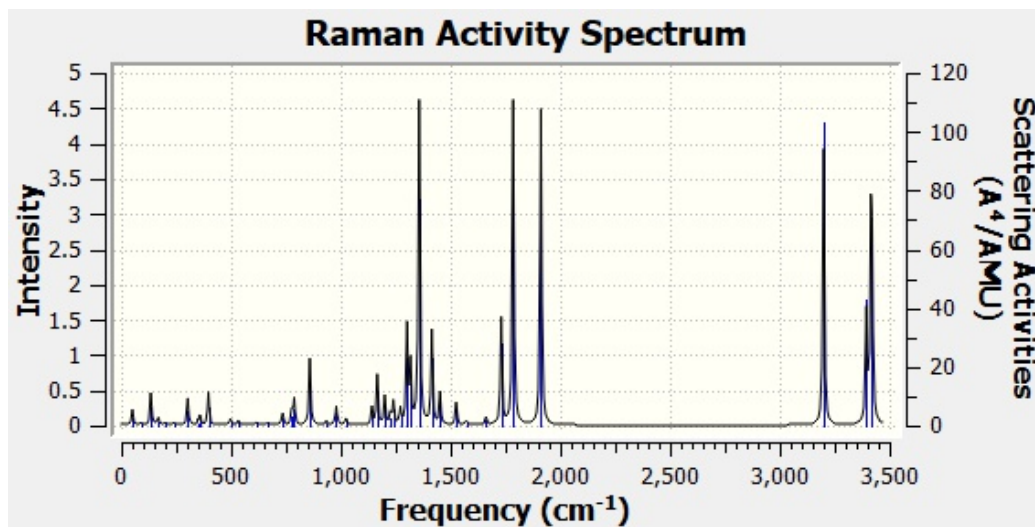


Figure 5

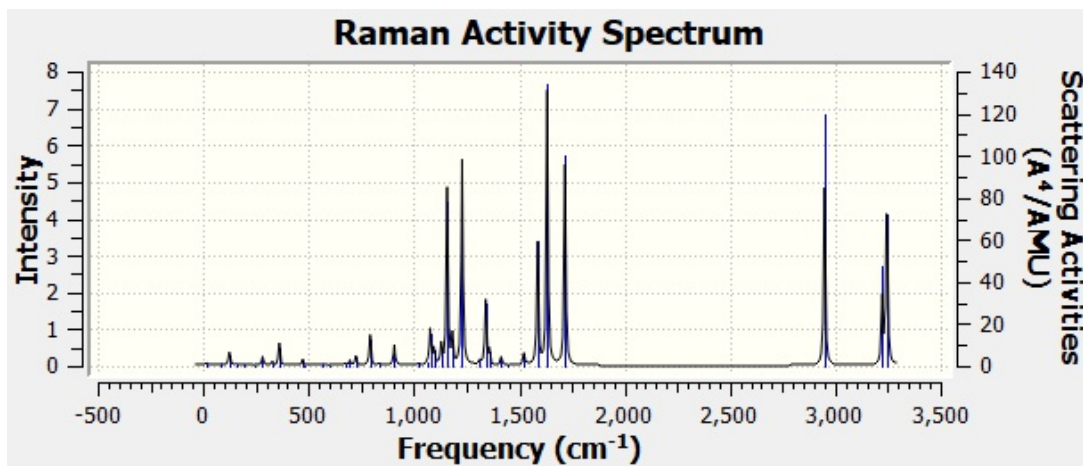


Figure 6

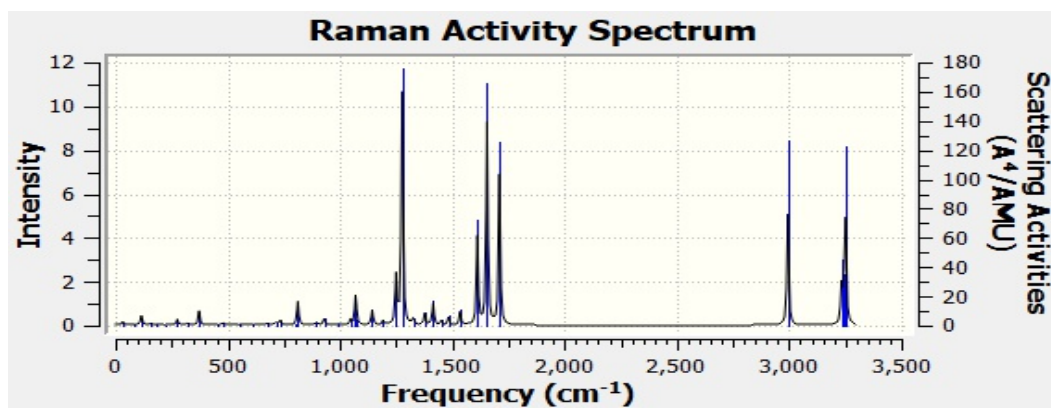


Figure 7

FRONTIER MOLECULAR ORBITALS The electronic absorption describes the transition from the ground state to the first excited state and is explained as one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The following figures 8 shows the HOMO-LUMO levels. The HOMO level is at -0.27324 a.u. and LUMO at -0.11305a.u. and the difference between the two levels is 0.16019a.u. which indicates a better stability of the compound.

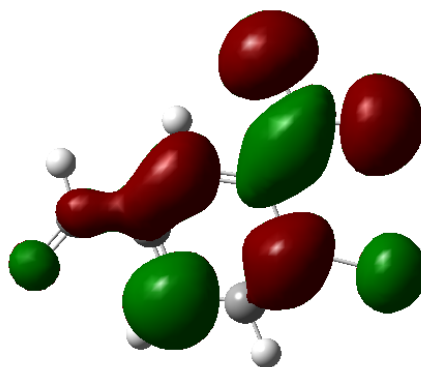


Figure 8

MOLECULAR ELECTROSTATIC POTENTIAL The molecular electro-static potential (MESP) is a pictorial representation of electrostatic potential shown on a constant electron density surface and it at the same time exhibits the molecular parameters as shape, size and electrostatic potential value represented in terms of colour coding. The different set of values of the electrostatic potential on the surface can be denoted by different colours as red colour depicts the region of the most electro-negative electrostatic potential, blue the region of the most electro-positive electrostatic potential, green the region of zero potential and yellow slightly electron rich region. This method represents the charge density on a molecule in a glance. In case of our reported compound the molecular electrostatic potential obtained by B3LYP/6-321G(d,p) is shown in figure 9.

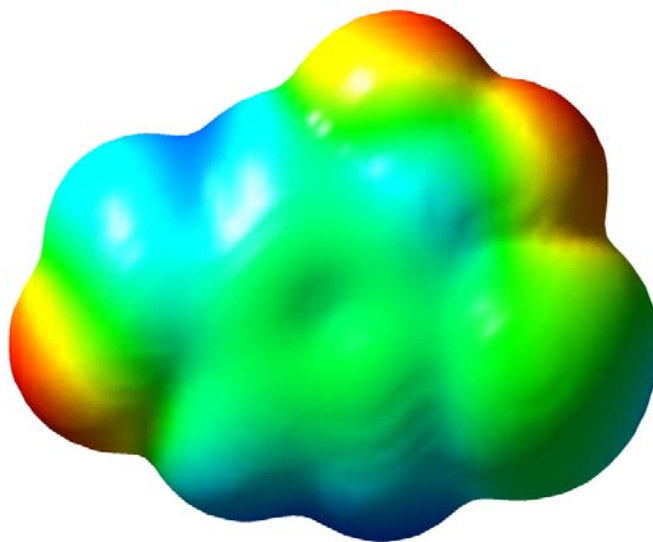


Figure 9

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