

Vibrational spectra of aniline in gas phase: An *ab-initio* study

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ABSTRACT

Vibrational frequencies of aniline in gas phase have been calculated and each of their modes of vibration assigned properly at RHF and DFT with 6-31G(d) basis set. In the present study, it has been observed that the 6-31G(d) basis set at both RHF and DFT levels of calculations provides better agreement to the experimental findings as compared to other basis sets. Simultaneously, Density functional theory is found to be superior to its counterpart Hartree Fock method.

Key words: Vibrational frequency, aniline, IR, HF, DFT, *Ab-initio*.

INTRODUCTION

In recent years, considerable efforts have been devoted to understand the vibrational spectra of simple aromatic compounds. The role of aromatic amines is of basic importance in biology and chemical industry, particularly aniline and its derivatives are used in the production of dyes, pesticides and antioxidants^{1,2}.

Some of the para-substituted derivatives of aniline are local anesthetics, and in these molecules the amino group plays an important role in the interaction with the corresponding receptor. Even in aniline, the amino group affects the planarity of the molecule and inclusion of an additional substituent group in aniline leads to further changes in the charge distribution in the molecule, and consequently affects the structural and vibrational parameters. Taking this into consideration it was thought worthwhile to calculate the vibrational frequencies of aniline at first stage in order to establish the appropriate method along with basis set so that it would be applied to its other derivatives to see upto which extent the substituents affects the structural and vibrational parameters.

Computational Detail

The entire calculations are performed at HF/6-31G(d) and Density functional Theory B3LYP/6-31G(d). All calculation in the present work were carried out in the Department of Physics, Paliwal Degree College Shikohabad on a Pentium IV PC using G03 and GAUSS VIEW 4.1 Version of *ab-initio* quantum mechanical program.³⁻¹³ The optimized structural parameters are used in the vibrational frequency calculations at the HF and DFT to characterize all stationary points as minima. We have utilized the gradient corrected density functional theory (DFT)¹⁴ with the three parameters hybrid function (B3 for the exchange part) and Lee-Yang-Parr (LYP) Correlation Function, accepted as a cost effective approach for the computation of molecular structure, vibrational frequencies and energies of optimized structures. Vibrational frequency assignments are made with a high degree of accuracy.

RESULTS AND DISCUSSION

Optimized Geometry

The optimized structure parameters of aniline calculated by HF/6-31G(d) and DFT B3LYP/

6-31G(d) along with some of their experimental values are listed in Table-1 and 2. The relative energies of aniline have also been calculated with different basis sets are presented in Table-3.

The optimized Hartree Fock C-N bond length (1.397 Å) is found to be less than the experimental value while in DFT calculations the same (1.400 Å) is in good agreement with the experimental observation (1.402 Å). Similar results have also been found for the N-H bond length. On the other hand the HF and DFT procedures give almost comparable magnitudes for the bond angles. Table-3 shows that basis set which includes the polarized function has the most stable form of energy.

In our study, vibrational frequencies calculated at HF/6-31G(d) and B3LYP/6-31G(d) level were scaled by 0.8929 and 0.9613, respectively. On the basis of the comparison between calculated and experimental results, assignment of fundamental modes were examined. The calculated frequencies are slightly lower than the experimental values for the majority of the normal modes. The infrared region of the electromagnetic spectrum extends from 14,000 cm⁻¹ to 10 cm⁻¹. The region of most interest for chemical analysis is the mid-infrared region (4,000 cm⁻¹ to 400 cm⁻¹) which corresponds to changes in vibrational energies within the molecules. We have used HF and DFT optimized geometries as the starting point to calculate vibrational frequencies of Aniline. The number of atoms (N) in aniline are 14 therefore there are 13 *stretching* vibrations and 23 *bending* modes according to formula (N-1) and 3N-6-(N-1). The assignments for calculated frequencies of aniline at DFT/B3LYP/6-31G(d) are listed in Table-4. The optimized structures and IR spectrum of aniline calculated at DFT/B3LYP/6-31G(d) level are shown in fig. 1(a) and 1(b)

N-H₂ Vibrations

The NH₂ *stretching* frequencies of aniline has been accurately determined by Nakanaga et. al¹⁵ using the infrared depletion spectroscopy. For the aniline these authors observed two absorption bands of approximately equal infrared intensities, positioned at 3508 and 3422 cm⁻¹. They assigned these bands to NH₂ antisymmetric and symmetric

stretching vibrations, respectively. As it is seen in Table-4 vibration 1 and 2 (V1 and V2) are assigned to N-H₂ *stretching* for B3LYP/6-31G(d) in the range of 3502 cm⁻¹ and 3408 cm⁻¹ for antisymmetric *stretching* and symmetric *stretching*, respectively, are in good agreement with the experimental values.

Evan¹⁶, in the IR spectroscopy studies of aniline in the gas phase and inert solvents, suggested that the two bands at 1115 and 1054 cm⁻¹ involve deformation vibrations. Our calculations for aniline clearly indicates that (V18 and V19) involves considerable contribution from the N-H *rocking* vibration. The calculated frequencies of these modes 1106 and 1037 cm⁻¹ are in better agreement with the corresponding experimental values.

C-N Vibrations

The *stretching* vibration has been assigned at 1282 cm⁻¹ in the IR spectrum of aniline by Gee et. al¹⁷. Our calculated frequency for this mode of vibration (V15) is found at 1265 cm⁻¹ which is in good agreement with the experimental value.

As is seen from Table-4 vibration (V25) also involves significant contribution from C-N *stretching* vibration. Michalska¹⁸ concluded that, in the IR spectrum of aniline, this vibration has been attributed to the band at 822 cm⁻¹ which is supported by our calculations.

The C-N *out of plane bending* vibration is coupled with ring torsions and belongs mainly to the vibration V36, V32, V27. For the aniline the calculated frequencies of these vibration are 215, 489, and 734 cm⁻¹, respectively are similar to experimental frequencies 217, 501 and 755 cm⁻¹, respectively.

Phenyl Ring Vibrations

The vibration V21 and V19 in aniline can be described as ring *in plane bending*, which originates from the C-C *stretching* vibrations coupled with C-H *in plane bending*. These modes of vibrations were assigned 972 and 1037 cm⁻¹, respectively are comparable with experimental values for aniline in argon matrix¹⁷. Both the modes of vibrations are very weak in infra red spectra in as predicted by calculations and illustrated in

Table1: Bond Length of Aniline At HF/6-31G(d)and B3LYP/6-31G(d)

S.No.	Parameters	Bond Length (HF)	Bond Length (DFT)	Exp.
1	C1-C2	1.3926	1.4052	1.397
2	C1-C6	1.3926	1.4052	
3	C1-N7	1.3973	1.4003	1.402
4	C2-C3	1.3835	1.3931	1.394
5	C2-H8	1.0766	1.0882	1.082
6	C3-C4	1.3855	1.3965	1.396
7	C3-H9	1.0759	1.0873	1.083
8	C4-C5	1.3856	1.3965	
9	C4-H10	1.0747	1.086	1.080
10	C5-C6	1.3834	1.3931	
11	C5-H11	1.0759	1.0873	
12	C6-H12	1.0766	1.0882	
13	N7-H13	0.9974	1.0128	
14	N7-H14	0.9974	1.0128	

Table 2: Bond Angle of Aniline At HF/6-31G(d) and DFT/B3LYP/631G(d)

S.No.	Parameters	Bond Angle	Bond Angle(DFT)	Exp
1	C2-C2-C6	118.7378	118.593	
2	C2-C1-N7	120.6094	120.674	
3	C6-C2-C7	120.6067	120.670	
4	C1-C2-C3	120.3874	120.471	120.12
5	C1-C2-H8	119.5887	119.417	
6	C3-C2-H8	120.0226	120.110	
7	C2-C3-C4	120.8622	120.785	120.70
8	C2-C3-H9	119.1773	119.176	
9	C4-C3-H9	119.9604	120.037	
10	C3-C4-C5	118.7627	118.893	
11	C3-C4-H10	120.6195	120.553	
12	C5-C4-H10	120.6178	120.553	
13	C4-C5-C6	120.8623	120.785	
14	C4-C5-H11	119.9593	120.038	
15	C6-C5-H11	119.1784	119.176	
16	C1-C6-C5	120.3874	120.471	
17	C1-C6-H12	119.5875	119.417	
18	C5-C6-H12	120.0238	120.111	
19	C1-N7-H13	114.2419	114.598	115.94
20	C1-N7-H14	114.2418	114.599	
21	H13-N7-H14	110.6417	111.041	113.10

Table 3: Energy and Dipole moment of Aniline by HF and DFT with different basis sets

Basis sets	Energy		Dipole Moment	
	HF	DFT	HF	DFT
6-31G(d)	-285.730882220	-287.60176074	1.5379	1.7131
6-31G+(d)	-285.74103810	-287.61612989	1.4800	1.6308
6-31G+(d,p)	-285.75787501	-287.63092745	1.4705	1.6314
6-31G++(d,p)	-285.75807403	-287.63113107	1.4647	1.6222

Table 4: Vibrational Frequencies of Aniline with HF/6-31G(d) and B3LYP/6-31G(d)

S. No.	6-31G(d)		Exp	Assignment
	HF	DFT		
V1	3469.89	3502.391	3508	N7-H13-H14 Anti symm Stretching
V2	3382.198	3408.212	3422	N7-H13-H14 Symm Stretching
V3	3024.618	3086.35	3072	C-H Symm Stretching
V4	3009.296	3069.364	3050	H8-C2-C3-H9 Symmetric Stretching
V5	3002.519	3063.894	3037	C-H Anti Symmetric
V6	2988.635	3048.600		H8-C2-C3-H9 and C5-H11-H12 Anti symm stre
V7	2986.831	3047.532	3025	H8-C2-C3-H9 and C5-H11-H12 Anti Symm Stre
V8	1645.499	1629.836	1618	N7-H12-H14 In plane bending (scissoring)
V9	1613.140	1603.814	1608	N7-H12-H14 In plane bending and C=C Stretching
V10	1599.461	1583.251	1594	C=C Stretching and C-H In plane bending
V11	1493.982	1492.178	1503	C-H Rocking
V12	1464.374	1460.878	1470	C-H In plane bending , C5=C6 and C2=C3 Stre
V13	1336.136	1324.566	1340	C-H In plane bending
V14	1245.525	1315.837	1324	C=C Ring Stretching
V15	1214.237	1265.667	1282	C-N Stretching
V16	1160.118	1164.759	1176	H9-C3-C2-H8 Scissoring
V17	1123.420	1143.889	1152	C-H In plane bending
V18	1067.605	1106.264	1115	N7-H13-H14 Rocking
V19	1029.612	1037.993	1054	C2-H8 In plane bending C3-C4 and C4-C5 Stre
V20	1009.129	1016.536	1028	Ring Compression and Expansion
V21	990.145	972.8644	996	C3-C4 and C4-C5 Stretching
V22	970.457	937.3348	968	C-H Out of plane bending
V23	968.725	910.726	957	C-H Out of plane bending
V24	885.613	884.4924	875	C-H Out of plane bending
V25	828.039	803.2142	822	C-N Stretching and C1-C2, C1-C6 Stretching
V26	796.645	795.3219	812	C-H Out of plane bending
V27	756.964	734.4332	755	Ring Compression and Expansion
V28	689.952	677.2935	688	C-H Out of plane bending
V29	645.414	611.3003	619	Ring Compression and Expansion
V30	608.359	608.3203		N7-H13-H14 Out of plane bending(wagg)C-NStre
V31	512.497	516.1316	526	Ring Compression and Expansion
V32	495.648	489.1383	501	C-H Out of plane bending
V33	408.251	401.9099	415	C-H Out of plane bending
V34	367.187	368.5816	390	N7-H13-H14 Rocking
V35	223.341	274.8837	277	N7-H13-H14 Rocking
V36	220.099	215.9176	217	C-N Out of plane bending

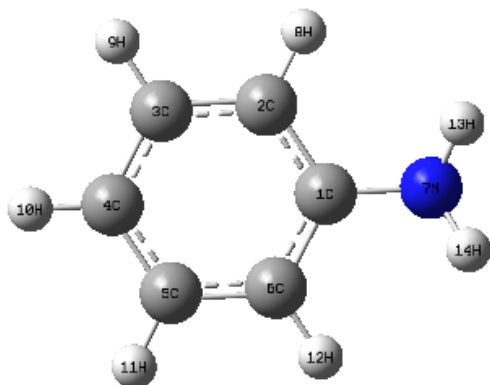
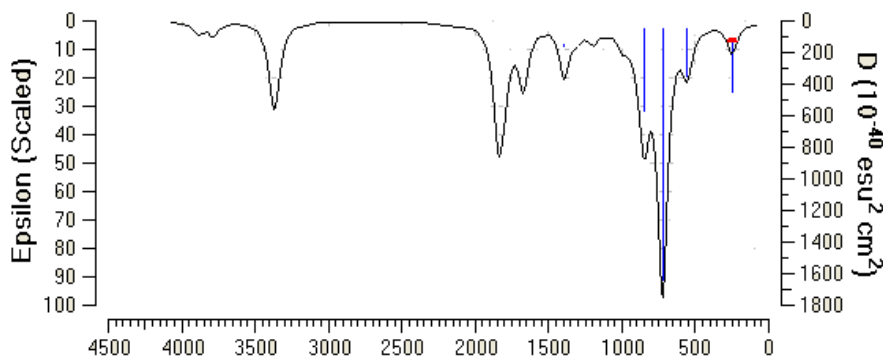


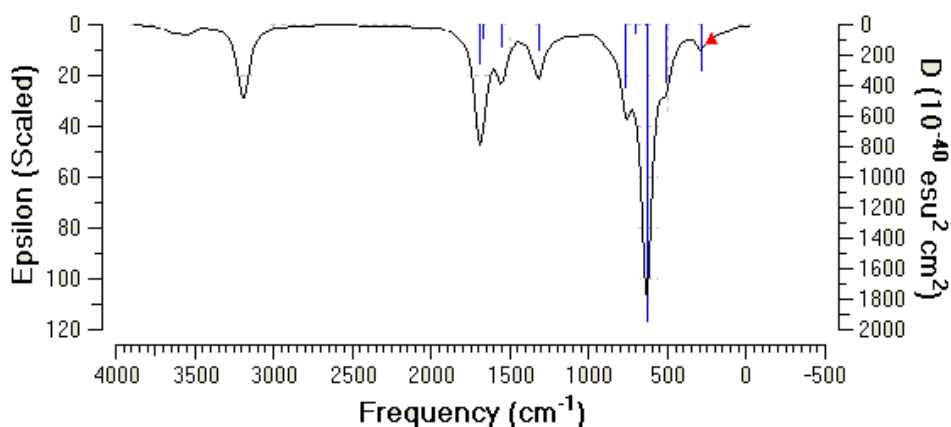
Fig 1(a): Optimized structure of aniline at B3LYP/6-31G(d)

fig1. The vibration V13 in the molecules can be described as the Kekule type vibration coupled with C-C *stretching* vibrations of the benzene ring. The B3LYP/6-31G(d) calculated frequencies of this mode 1324 cm^{-1} is in very good agreement with the experimental 1340 cm^{-1} reported by Evans¹⁶.

According to calculations, vibration V3 has been longest Raman scattering due to C-H *stretching* vibrations. The frequencies of these vibrations is in good agreement with experimental values. The calculated frequencies of modes V7 and V6 (3047 and 3048 cm^{-1}), respectively, indicate that the corresponding anisymmetric stretching bands may overlap in vibrational spectra of aniline.



IR Spectra of Aniline at HF/6-31G(d)



IR Spectra of Aniline at DFT/B3LYP/6-31G(d)

Fig. 2:

CONCLUSIONS

The HF/6-31G(d) and DFT/B3LYP/6-31G(d) calculations were performed for aniline molecule in gas phase. The calculated results show that predicted geometry can well reproduce the structural parameters. Scaled vibrational frequencies and their normal modes of vibration have been compared with experimental observations. It was found that DFT B3LYP/6-31G(d) method provides more satisfactory results as compared to HF/6-31G(d) because of the fact that Hartree Fock provides an inadequate treatment

of the correlation between the motions of the electrons within a molecular systems especially that arising between electrons of opposite spin that remains uncorrelated. On the other hand the DFT approach is based upon a strategy of modeling electron correlation via general functionals of the electron density. The encouraging results so obtained lead us to apply the present procedure for other biologically, chemically and medicinally important derivatives of aniline in order to study the finer details affecting their structural and vibrational behaviour.

REFERENCES

1. Whysner J, Vera L & Williams G M, *Pharmaco, Ther*, **71**: 107 (1996).
2. Hohenberg P & Kohn W, *Phys Rev*, B **136**: 864 (1964).
3. Gaussian 03 Revision D.I., Frich M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Montgomery J. A., Jr., Vreven T., Kudin K. N., Burant J.C., Millam J. M., Iyengar S. S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G. A., Nakajima H., Hada M., Kitao O., Nakai H., Klene M., Li X., Knox J. E., Hratchian H. P., Cross J. B., Bakken, V., Admo C., Jaramillo J., Comperts R., Stratmann, R. E., Yazyev O., Austin A. J., Cammi R., Pomelli, C., Ochterski J. W., Ayala P.Y., Morokuma K., Voth G.A., Salvador P., Dannenberg J. J., Zakrzewski V. G., Dapprich S., Danniels A..D., Strain M.C., Farkas O., Malick D.K., Rabuck A.D., Stefanov B. B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R. L., Fox D. J., Keith T., Al-Laham M. A. Raghavachari K., Forcesman J. B., Ortiz J. V., Cui Q., Cioslowski J., Peng C.Y., Nanayakkara A., Challacombe M., Gill P. M. W., Johnson B., Chen W., Wong M. W., Gonzalez C., and Pople J. A., Gaussian Inc, Wallingford (2005).
4. Hartree-Fock Frequencies: J.A. Pople, R.Krishnan H.B.Schlegel, D. DeFrees, J.S. Binkley, M.J. Frisch, R.F. Whiteside, R.F. Hout, and W.J. Hehre, *Int. J. QuantumChem., Symp.*, **15**: 269 (1981).
5. P. Hohenberg and W. Kohn, *Phys. Rev*, **136**: B864 (1964).
6. W. Kohn and L. J. Sham, *Phys., Rev.* **140**: A1133 (1965).
7. The Challenge of d and f Electrons, Ed. D. R Salahub and M. C. Zerner (ACS, Washington D.C., 1989).
8. R. G. Parr and W. Yang, *Density- functional theory of atoms and molecules* (Oxford Univ. Press, Oxford, 1989).
9. M. Head-Gordon, J. A. Pople, and M. J. Frisch, *Chem.Phys Lett.* **153**: 503 (1988).
10. M. J. Frisch, M. Head-Gordon, and J. A. Pople, *Chem. Phys. Lett.* **166**: 275 (1990).
11. M. J. Frisch, M. Head-Gordon, and J. A. Pople, *Chem.Phys. Lett.* **166**: 281 (1990).
12. R.H. Nobes, J.A. Pople, L. Ranom, N.C. Handy, P.J.Knowles, *Chem Phys. Lett.*, **138**: 481 (1987).
13. H.B. Schlegel, *J. Comp. Chem.* **3**: 214 (1982).
14. DFT Frequencies and ZPE: M.W. Wong, *Chem, Phys. Lett.*, in Press. (1996).
15. T. Nakanaga, F. Ito, J. Miyawaki, K. Sugawara, and H. Takeo, *Chem. Phys. Lett.* **261**: 414 (1996).
16. J. C. Evans, *Specrochim. Acta* **16**: 428 (1960).
17. Ch. Gee, S. Douin, C. Crepin, and Ph. Brechigiac, *Chem. Phys.Lett.* **338**: 139 (2001).
18. Piotr M. Wojciechowski, Wiktor Zierkiewicz,

- and Danuta Michalska. *Journal of Chemical Phys.* **118**: 10900-10911(2003)
19. Belgin BARDAKCI, *Journal of Arts and Sciences SayiL7,Mayis*, 13-19 (2007).
20. Rakesh Kumar, A.K. Sharma, S.D.S. Chauhan, D. Kulshreshtha, R.Gupta, P.K.S. Chauhan, O.P. Singh, *Material Science Research India* **6**(2): 551-558 (2009).
21. A.K. Sharma, S.D.S. Chauhan, Rakesh Kumar, D. Kulshreshtha, R.Gupta, P.K.S. Chauhan, O.P. Singh, *Material Science Research, India* **6**(2): 423-430 (2009).
22. A .A. El-Barbary, M.M. El-Nahass, M. A . Kamel, M.A.M. El-Mansy. *Journal of Applied Sciences Research*, **5**(11): 1977-1987 (2009).