Spectroscopic Studies and Vibrational Assignments, Homo-Lumo, UV-VIS, NBO Analysis of Benzonitrile

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Abstract : The Fourier transform infrared and FT-Raman spectra of Benzonitrile have been recorded in region of 4000-400 and 4000-100 cm^{-1} respectively. A complete assignments and analysis of fundamental vibrational modes of the molecule have been carried out. The observed fundamental modes have been compared with harmonic vibrational frequencies computed using ab initio and density functional theory calculations by employing B3LYP functional at 6-311G(d, p) level and HF/6-311G(d, p).UV-Vis spectrum of the compound has been recorded, the natural bond orbital (NBO) electronic properties, such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies have been calculated with B3LYP/6-311G(d, p) level. These calculated energies show that charge transfer occurs within molecule. NBO analysis, thermodynamics properties and Mulliken charges of the title molecule are also calculated and interpreted.

Keywords : Benzonitrile, DFT, HF, HOMO-LUMO, UV-VIS, NBO.

1. Introduction:

Benzonitrile is the chemical compound with the formula C6H5CN, other names are phenyl cyanide (PhCN) and cyanobenzene. The systematic IUPAC name is Benzenecarbonitrile. This aromatic organic compound is a colourless liquid used as intermediate for rubber chemicals; solvent for nitrile rubber, specialty lacquers, and many resins and polymers, and for many anhydrous metallic salts It is mainly used as a precursor to the resin benzoguanamine. Pharmaceutical and Agrochemical Intermediates. It is the best solvent in the chemical and physical laboratories [1-3].

2. Experimental details:

The Fourier transform Infrared spectrum and Fourier transform Raman spectrum of the molecule were taken from SDBS [4] recorded in the region 400-4000 cm^{-1} and 100-4000 cm^{-1}.

3. Computational Details

In the present work, the density functional method (DFT) has been employed using Becke's three parameter hybrid exchange functional with the Lee-Yang –Parr correlation functional to optimize the structure of the molecule and to calculate the electronic structure of the title molecule [5]. The entire calculations were performed at ab-initio Hartree -Fock(HF) and DFT method using B3LYP levels at 6-31 G(d,p) basis sets on a Pentium V/ 1.6 GHz personal computer using Gaussian 09W program package [6] and applying geometry optimization Initial geometry generated was minimized at the Hartree Fock level using 6-311 G (d,p) basis set. The vibrational modes are assigned using Gauss-View molecular visualization program package. The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima.

4. Results and Discussion

4.1 Molecular geometry

The optimized structural parameters of Benzonitrile calculated by HF and DFT/ B3L YP levels with 6-311G(d, p) basis sets are listed in the Table. 1 and Table.2 in accordance with the atom numbering given in Fig.1.

In the table compares the calculated bond angles and bond lengths with experimental data. Benzonitrile is mono- substituted aromatic compound and the substituent is cyanogen group. The bond length between the carbon atoms to hydrogen atoms is small compared to the bond length between the 8C carbon atom to 1N nitrogen atom and carbon to carbon atoms. The largest bond length is 2C-8C carbon atom.
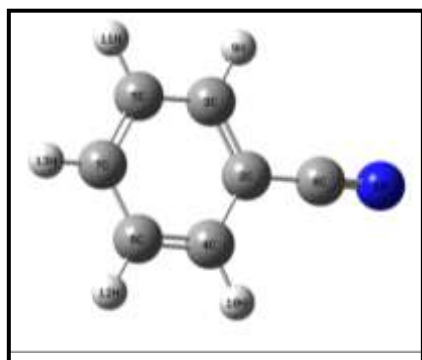
Fig.1. Molecular structure of Benzonitrile with atomic numbering

Table 1 Optimized Geometrical parameters (bond length) of Benzonitrile

S.NO	OPTIMIZED PARAMETERS	BOND LENGTH(Å)	
		B3LYP/6-311G(d, p)	HF/6-311G(d,p)
1	N1-8C	1.155	1.1307
2	2C-3C	1.4021	1.3891
3	2C-4C	1.4021	1.3891
4	2C-8C	1.4314	1.4432
5	3C-5C	1.3897	1.3821
6	3C-9H	1.0829	1.074

7	4C-6C	1.3897	1.3821
8	4C-10H	1.0829	1.074
9	5C-7C	1.3942	1.3854
10	5C-11H	1.0836	1.0745
11	6C-7C	1.3942	1.3854
12	6C-12H	1.0836	1.0745
13	7C-13H	1.0839	1.075

Table 2 Optimized parameters (bond angle) of Benzonitrile.

SI.NO	OPTIMIZED PARAMETERS	BOND ANGLE (º)	
		B3LYP/6-311G(d, p)	**HF/6-311G(d, p)**
1	3C-2C-4C	120.006	120.49
2	3C-2C-8C	119.997	119.755
3	4C-2C-8C	119.997	119.755
4	2C-3C-5C	119.743	119.575
5	2C-3C-9H	119.57	119.756
6	5C-3C-9H	120.688	120.669
7	2C-4C-6C	119.743	119.575
8	2C-4C-10H	119.57	119.756
9	6C-4C-10H	120.688	120.669
10	3C-5C-7C	120.19	120.031
11	3C-5C-11H	119.675	119.78

4.2 Vibrational assignments

The studied molecule have 13 atoms and it has 33 normal modes of vibration. The detailed vibrational analysis of fundamental modes using B3LYP/6-311G(d, p) and HF/6-311G(d, p) with FT-IR and FT-Raman was calculated by Gaussian 09W. The experimental frequencies of FT-IR and FT-Raman taken by SDBS (Spectral Database for Organic Compound) are tabulated in Table.3 and Fig.2 and Fig.3. The Vibrational assignments are based on the observation of the animated modes in gauss view and assignments reported in literature. The calculated vibrational wave numbers are usually higher than the corresponding experimental quantities because of the combination of electron correlation effects and basis sets deficiencies. For DFT/B3LYP and HF levels with 6-311G(d, p) basis set, the wave numbers are scaled with 0.97 and 0.99 respectively [7].

Table .3 Vibrational assignments of Benzonitrile

Observed Wave number		Calculated Wave number		Vibrational assignment	IR Intensity		Raman Activity	
FT-IR cm^{-1}	FT-RAMAN cm^{-1}	DFT B3LYP/ 6-311G(d, p)	HF 6-311G(d, p)		DFT	HF	DFT	HF
		3105.94	3330.36	υ_{sy} (C$_4$-H$_{10}$)	2.91	4.03	313.32	290.2
		3103.03	3326.4	υ_{sy} (C$_3$-H$_9$)	9.66	13.65	1.92	0.94
		3094.3	3316.5	υ_{sy}(C$_7$-H$_{13}$)	11.6	15.85	68.33	51.01
3088		3086.54	3307.59	υ_{sy}(C$_3$-H$_9$)	4.64	4.98	123.04	110.97
3066	3078	3075.87	3295.71	υ_{sy}(C$_7$-H$_{13}$)	0.02	0.08	43.85	41.25
2256	2230	2269.8	2559.15	υ_{sy}(N$_1$-C$_8$) υ_{sy}(C$_2$-C$_8$)	26.36	47.74	348.03	269.26
1682	1600	1594.68	1773.09	υ_{sy}(C$_4$-C$_6$)	0.89	1.14	76.78	69.93
1572	1524	1567.52	1745.37	υ_{sy}(C$_2$-C$_3$) ε(C$_4$-C$_6$-C$_7$)	1.22	0.58	2.59	2.92
1477		1478.28	1631.52	ε (H$_{11}$-C$_5$-C$_7$)	10.22	17.94	2.44	0.76
1441		1432.69	1578.06	ε(H$_{13}$-C$_7$-C$_6$)	7.88	11.43	1.49	0.99
1336		1314.35	1442.43	γ(H$_{10}$-C$_4$-C$_6$)	0.89	0.57	1.88	1.26
1288		1281.37	1310.76	υ(C$_2$-C$_3$)	1.36	2.75	0.09	0.16
1178	1194	1183.4	1281.06	υ_{sy}(C$_3$-C$_5$) ε(C$_2$-C$_3$-C$_5$)	0.39	0.07	32.12	19.75
1163	1179	1164.97	1270.17	ε(H$_9$-C$_3$-C$_5$)	1.01	1.4	12.25	16.19
		1151.39	1192.95	υ_{sy}(C$_6$-C$_7$) ε(H$_{13}$-C$_7$-C$_6$)	0.15	8.46	4.93	6.24
1072		1070.88	1157.31	υ_{sy}(C$_4$-C$_6$) ε(H$_9$-C$_3$-C$_5$)	4.12	0.05	0.35	0.47
1001	1002	1017.53	1113.75	υ_{sy}(C$_5$-C$_7$) ε(H$_{11}$-C$_5$-C$_7$) γ(C$_4$-C$_6$-C$_7$)	3.6	0	8.22	0.28
989		985.52	1105.83	υ_{sy}(C$_6$-C$_7$) ε(C$_4$-C$_6$-C$_7$)	0.2	2.9	35.67	5.96
		983.58	1093.95	τ (H$_{11}$-C$_5$-C$_7$-C$_6$)	0.04	0	0.17	0
946		958.36	1072.17	τ (H$_9$-C$_3$-C$_5$-C$_7$)	0	0.05	0	38.14
927		916.65	1043.46	τ (H$_{10}$-C$_4$-C$_6$-C$_7$)	2.95	3.19	0.77	0.45
846		832.26	942.48	τ (H$_{12}$-C$_6$-C$_7$-C$_5$)	0	0	0.96	0.12

768		756.6	846.45	τ (H$_{11}$-C$_5$-C$_7$-C$_6$) τ (C$_2$-C$_3$-C$_5$- C$_7$) ρ_O(C$_8$-C$_3$-C$_4$- C$_2$)	37.97	48.25	0.21	1.07
773		749.81	808.83	υ(C$_8$-C$_2$) ε(C$_6$-C$_7$-C$_5$)	2.25	3.63	9.06	8.49
688		683.85	753.39	τ (H$_9$-C$_3$-C$_5$-C$_7$) τ (C$_4$-C$_6$-C$_7$- C$_5$)	37.85	41.23	0.15	0.42
625		619.83	678.15	υ_{sy}(C$_2$-C$_3$) ε(C$_4$-C$_6$-C$_7$)	0.16	0.3	3.57	2.82
570		557.75	621.72	ρ_O(C$_8$-C$_3$-C$_4$-C$_2$) τ (C$_6$-C$_7$-C$_5$- C$_3$) τ(N$_1$-C$_8$-C$_2$- C$_3$)	18.57	21.86	2.98	5.01
548		552.9	613.8	τ(N$_1$-C$_8$-C$_2$-C$_3$) ε(C$_8$-C$_2$-C$_4$) ω(N$_1$-C$_8$-C$_2$)	0.21	0.65	2.82	5.55
466	463	452.02	488.07	ε(C$_2$-C$_3$-C$_5$) υ_{sy}(C$_8$-C$_2$)	0	0.07	5.65	4.65
		395.76	441.54	τ (C$_6$-C$_7$-C$_5$-C$_3$)	0	0	0	0
392		380.24	427.68	τ (C$_4$-C$_6$-C$_7$-C$_5$) τ(N$_1$-C$_8$-C$_2$- C$_3$)	0.47	0.57	2.37	2.94
168	173	162.96	185.13	τ(N$_1$-C$_8$-C$_2$-C$_3$) ε(C$_8$-C$_2$-C$_4$) t(N$_1$-C$_8$-C$_2$)	4.29	5.64	3.36	3.24
145		140.65	160.38	ρ_O(C$_8$-C$_3$-C$_4$-C$_2$) τ (C$_6$-C$_7$-C$_5$- C$_3$) τ(N$_1$-C$_8$-C$_2$- C$_3$)	1.64	1.91	0.76	0.63

Abbreviations used: υ-stretching, υ_{sy}-symmetric stretching, υ_{asy}-asymmetric stretching ρ- bending, ρ_O-out of plane, ρ_i-in plane bending, ε- scissoring, γ-rocking, t-twisting, ω-wagging, τ-torsion

Fig.2. FT-IR spectrum of Benzonitrile

Fig.3. FT-RAMAN spectrum of Benzonitrile
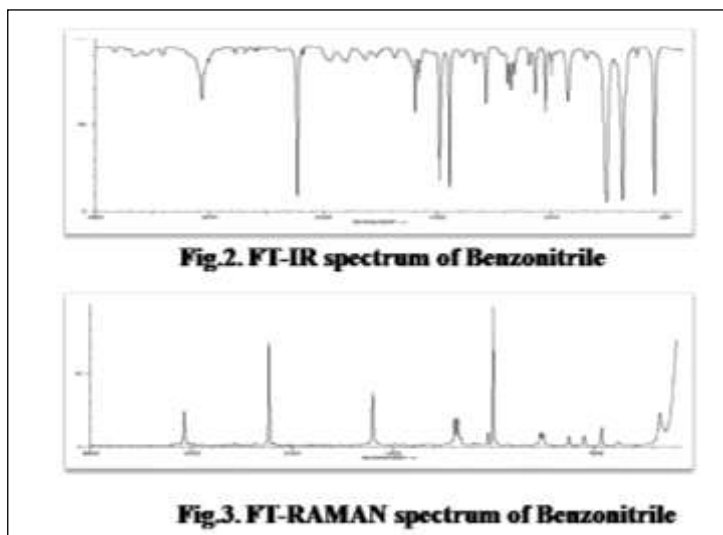
C-H and C-C vibrations

The most characteristic vibrations are those of C-H and C-C stretching and bending. The bonding of CH_3 or CH_4 to atoms other than carbon or carbonyl group or aromatic or hetroaromatic ring may cause appreciable shifts the C-H stretching and bending frequencies [8].

C-H Vibrations:

The hetero aromatic structure shows the presence of C-H stretching vibrations in the region 3250–3000 cm^{-1} which is the characteristic region for the ready identification of C-H stretching vibrations. In this region, the bands are not affected appreciably by the nature of substituent [9-11]. The C-H stretching modes usually appear with strong Raman intensity and are highly polarized. In present study, the C-H stretching frequencies are observed in FT-IR at 3066cm^{-1} and 3078cm^{-1} in FT-Raman. The B3LYP/6-311G(d, p) methods give at 3103, 3094, 3086 and 3075$cm^{-1}$and HF/6-311G(d, p) at 3295cm^{-1}. C-H in plane bending vibrationsappear in the range 1300–1000 cm^{-1} in present work C-H in plane bending frequencies are appear in 1163, 1072, 1001cm^{-1} at FT-IR and FT-Raman appear at 1179 and 1002cm^{-1}. The theoretical calculated vibrations of C-H observed at 1164, 1070 and 1017cm^{-1} in B3LYP/6-311G(d, p) and HF/6-311G(d, p) at 1270, 1192, 1157 and 1113cm^{-1}. The C-C-C-H Torsion vibrations are generally observed in the region 800-1200cm^{-1}. The C-C-C- H torsion vibration was observed in FT-IR spectrum at 946, 927and 846cm^{-1}. The calculated values in B3LYP/6-311G(d, p) at 983, 958, 916 and 832cm^{-1}. HF/6-311G(d, p) at 1093, 1072, 1043, 942 and 846cm^{-1}.

C-C and C-C-C Vibrations:

In benzonitriles, the distance between two carbon atoms changes the ring angles because of its substituent groups such as cyanogen. There are six equivalent C-C bonds in benzene and consequently there will be six C-C stretching vibrations [11]. The C-C stretching frequencies are generally predicted in the region 1650-650cm^{-1}. In our present study, C-C stretching vibrations are observed at 1572, 1288, 1178, 1072, 1001, 773 and 625cm^{-1}in FT-IR spectrum and 1600 1524, 1194 and 1002cm^{-1}in FT-Raman. The theoretical C-C stretching vibrations are found at 1594, 1567, 1281, 1183, 1151, 1070, 1017 and 749cm^{-1} in B3LYP/6- 311G(d, p) and at 1310, 1281, 1192, 1157, 1113, 808 and 678cm^{-1} in HF/6-311G(d, p).The C-C-C in plane bending frequencies are observed in the region 1500-464cm^{-1}. For the benzonitrile

compound is assigned at 1572, 1178, 989, 773 and 625cm^{-1} in FT-IR and FT-Raman at 1524 and 1194cm^{-1}. The comparison of calculated and values are assigned at 1567,1183, 985, 749 and 619cm^{-1} in DFT/B3LYP and HF/6-311G(d, p) at 1281, 1105, 808 and 678cm^{-1}. The theoretically calculated C-C-C out-of-plane has been found to be consistent with the recorded spectral values. For the titled compound C-C-C-C Torsion vibration was observed in the FT-IR at 768, 688, 570, 392 and 145cm^{-1}. The calculated DFT/B3LYP at 756, 683, 557, 395, 380, 140 and HF/6-311G(d, p) at 846, 753, 621, 441, 427 and 160cm^{-1}.

C=C vibration:

Unconjugated C=C vibration bands have stretching frequency in the region 1620-

1680 cm-1 for alkenes. Conjugation of the C=C bond with a double bonds or an aromatic rings decrease the frequency of the bond. In our present compound have three C=C symmetric vibrations [10-11]. The calculated value was at 1682 and 1572cm^{-1} for FT-IR and 1600 and 1524cm^{-1} for FT-Raman. They were calculated as 1594 and 1567 cm-1 for B3LYP method.

C-N vibration:

A C-N group attached to the ring, a band of good intensity has been absorbed in the region 2240–2221 cm^{-1} and it is being attributed to C-N stretching [12]. In the case of benzonitrile the C≡N stretching mode appears in our calculation at 2256 cm^{-1} (FT-IR) and 2230 cm^{-1} (FT-Raman). The theoretical C≡N stretching vibrations are found at 2269 cm^{-1} in B3LYP/6-311G(d, p) and HF/6-311G(d, p) at 2559cm^{-1}. For the tittle compound N-C-C-C out of plane bending was observed in the FT-IR spectrum at 548, 168 cm-1 and 173cm^{-1} in FT-Raman. The theoritial N-C-C-C out of bending was observed at 552cm^{-1} in B3LYP/6- 311G(d, p) and HF/6-311G(d, p) at 613cm^{-1}. The N-C-C-C torsion vibration are generally 580-170cm^{-1}. For our compound the N-C-C-C torsion vibration are observed in the FT-IR at 570, 548, 392 and 168cm^{-1} and FT-Raman at 173cm^{-1}. These experiment values are well agreement with the calculated frequencies.

5. HOMO LUMO Analysis

Highest occupied molecular Orbital HOMO and Lowest Unoccupied Molecular Orbital LUMO are very important parameters for quantum chemistry [39]. The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that largely acts as an electron acceptor. The energies of HOMO, LUMO, LUMO+1 and HOMO-1 and their orbital energy gaps of 5, 6, 7, 8-tetrahydro-2-naptholare calculated using B3LYP level with 6-31+G(d,p)method and the pictorial illustration of the frontier molecular orbital's and their respective positive and negative regions are shown in Fig. 4. Molecular orbital's, when viewed in a qualitative graphical representation, can provide insight into the nature of reactivity, and some of the structural and physical properties of molecules.

The positive and negative phase is represented in red and green colour, respectively. From the plots we can see that the regions of HOMO and LUMO levels spread over the entire molecule and the calculated energy gap of HOMO- LUMO explains the ultimate charge transfer interface within the molecule [13].

The power of an electronegative atom in a compound to attract electron towards it was introduced by Pauling Hardness η, ionization potential I, electronegativity χ, chemical potential μ, electron affinity A, global softness σ and global electrophilicity ω. are defined follows,

All the calculated values of quantum chemical parameters of the molecules in RB3LYP method with 6-311G(d,p)basis set was presented in the Table 4.

Ionization potential $(I_P) = -E_{HOMO}$

Electron affinity $(E_A) = -E_{LUMO}$

Global hardness$(\eta) = \left(\dfrac{-E_{HOMO} + E_{LUMO}}{2}\right)$

Global softness$(S) = 1/2\eta$

Electronegativity $(\chi) = -\left(\dfrac{E_{HOMO} + E_{LUMO}}{2}\right)$

Chemical potential or Fermi energy$(\mu) = -\chi = \left(\dfrac{E_{HOMO} + E_{LUMO}}{2}\right)$

Electrophilicity$(\omega) = \mu^2/2\eta$

Table.4 HOMO-LUMO energy values of Benzonitrile

Molecular properties	Calculated Energies (B3LYP/6-311 G(d, p))	
	In a.u.	In eV
HOMO(E_{HOMO})	-0.2760	-7.51023
LUMO(E_{LUMO})	-0.06178	-1.6812
Energy gap(ΔE)	0.21422	5.8291
Ionization potential (I_P)	0.2760	7.5102
Electron affinity (E_A)	0.06178	1.6811
Global hardness(η)	0.1155	3.1442
Global softness(S)	4.3290	117.7964
Electronegativity (χ)	0.16045	4.3660
Chemical potential or Fermi energy(μ)	-0.16045	-4.3660
Electrophilicity(ω)	0.1114	3.0313
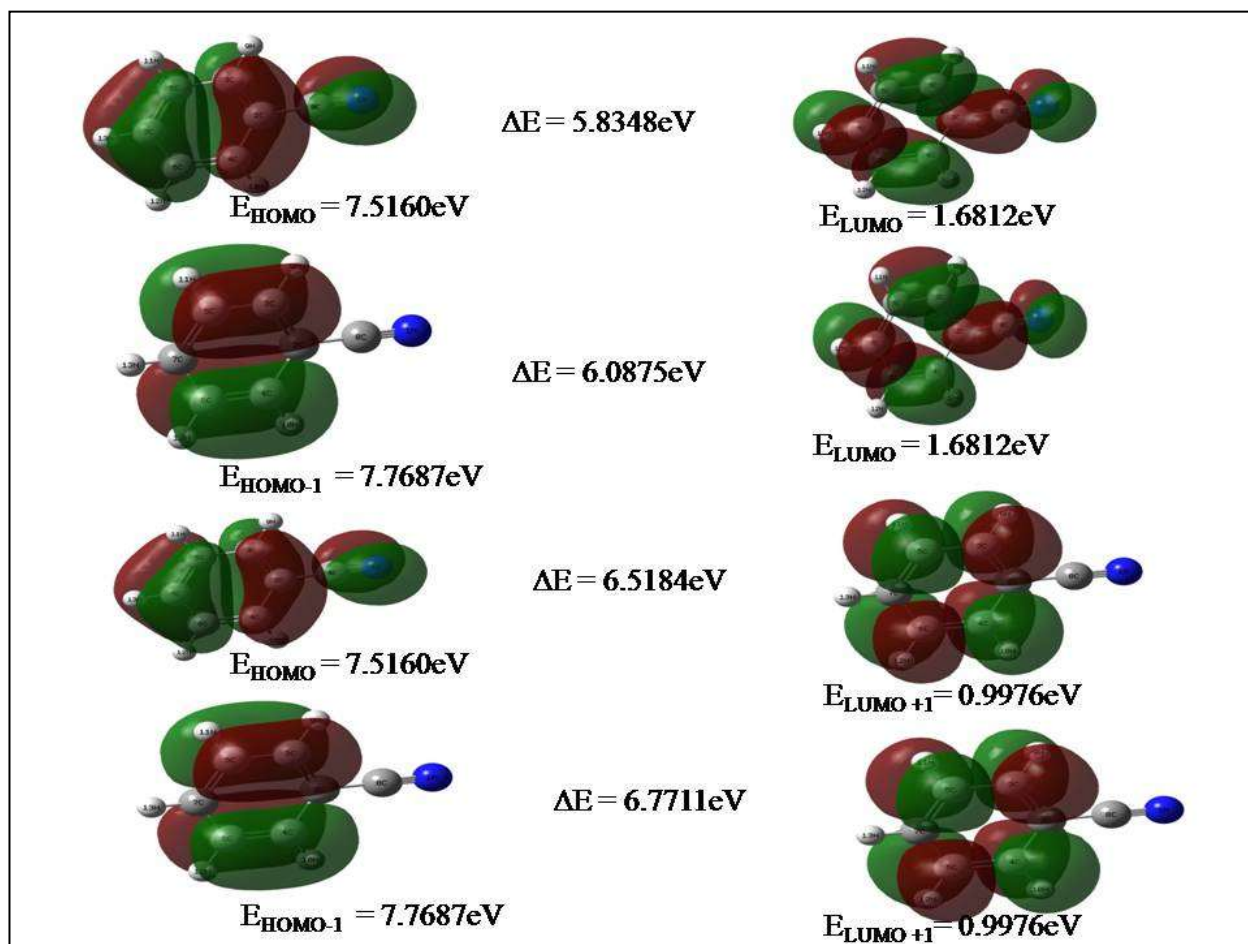
Fig.4. The atomic orbital components of the HOMO-LUMO for Benzonitrile

6. UV-Visible spectral studies

The theoretical UV absorption spectrum of benzonitrile is shown in Fig.5 due to Franck-Condon principle, the maximum absorption peak in an UV-Vis spectrum corresponds to vertical excitation. The maximum absorption wavelength corresponds to the electronic transition from the HOMO to LUMO. In the UV-Vis region with high extinction coefficients,

All molecules allow π-π* and σ-σ * transition [14.]. The UV-Vis electronic spectrum of the molecule,

their energies was calculated by TDSCF and the results are tabulated in Table.5.

In pure benzene ring the allowed transition is at 180 nm, in the present compound, computed data is 220nm respectively which was obtained by TDSCF B3LYP/6-311G(d,p) method. This is due to the presence of the cyanide group. The analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state. It is mainly described by an electron excitation from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [15]. The HOMO energy characterizes the ability of electron donating LUMO characterizes the ability of electron accepting and the gap between HOMO and LUMO characterizes the molecular chemical stability. The HOMO-LUMO energy gap in pure benzene is 6.6221 eV, whereas, the energy gap in our title molecule is reduced to 5.8348 because of present the cyanide group on the benzene ring.
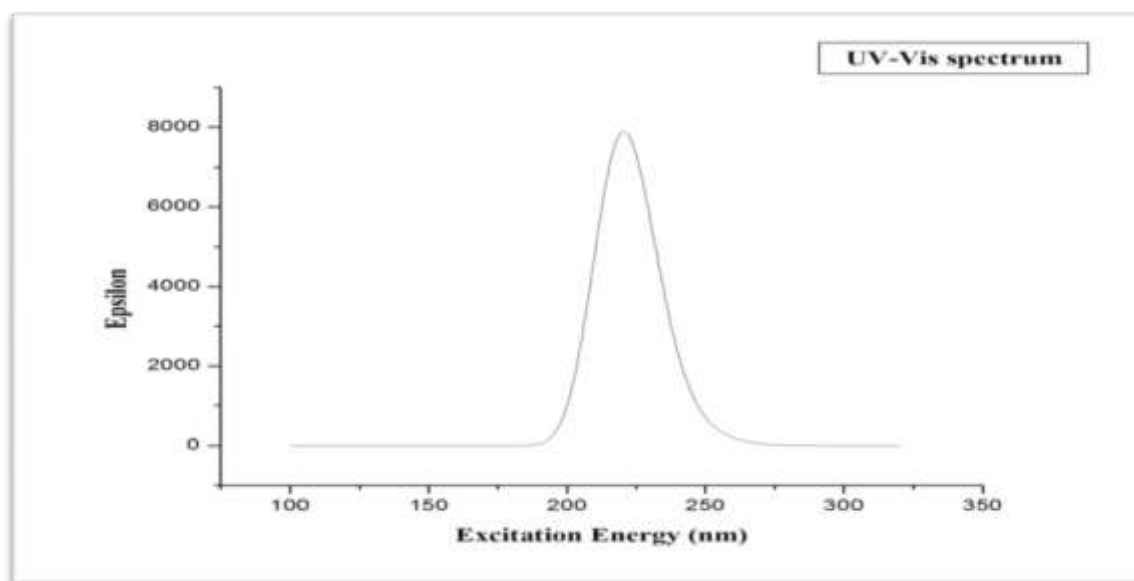
Fig 5. UV-Visible spectrum of Benzonitrile

Table. 5 Calculated Absorption Wavelength Oscillator Strength of Benzonitrile

Excitation	Singlet A	Energy (eV)	Max	Oscillator Strength	Transition
Excited State1					
26 -> 28	0.55753	5.1260	241.87	0.0064	HOMO-1→LUMO
27 -> 29	-0.43244				HOMO→LUMO+1
Excited State 2					
25 -> 31	-0.10470	5.6261	220.37	0.1933	HOMO-2→LIMO-3
26 -> 29	0.24797				HOMO-1→LUMO+1
27 -> 28	0.65238				HOMO→LUMO
Excited State 3					
25 -> 28	0.69555	6.2676	197.82	0.0000	HOMO-2→LUMO

7. NBO Analysis:

Natural bond orbital (NBO) analysis provides an efficient method for studying intra and intermolecular bonding and interaction among bonds and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems [16]. NBO theory also allows the assignment of the hybridization of atomic lone pairs and of the atoms involved in bond orbitals. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulted from the second-order micro-disturbance theory are reported. The second-order Fock matrix is carried out to evaluate the donor–acceptor interactions in NBO analysis. The results of interactions are the loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy $E^{(2)}$ associated with the delocalization i→j is estimated as

$$E^{(2)} = E_{ij} = q_i \frac{F_{i,j}^2}{\varepsilon_i - \varepsilon_j}$$

Where, q_i is the donor orbital occupancy, ε_i and ε_j the diagonal elements and F(i, j) is

the off diagonal NBO Fock matrix element. The second order perturbation theory analysis of Fock matrix in NBO shows strong intermolecular hyper conjugative interactions, which are Presented in Table.6. The larger the E(2) value, the more intensive is the interaction between electron donors and electron acceptors i.e., the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (anti-bond or Rydberg) non-Lewis NBO orbitals corresponds to a stabilizing donor–acceptor interaction [17-20].

Table. 6 NBO Analysis of Benzonitrile.

Donor	ED/e	Acceptor	ED/e	E(2)[a](Kcal/mol)	E(j)-E(i)[b](a.u)	F(i,j)[c](a.u)
σ N1-C8	1.99392	σ* C2-C8	0.01207	11.34	2.13	0.140
σ C2-C8	1.97710	σ * N1-C8	0.01207	13.20	2.16	0.151
π C2-C4	1.66050	π* N1- C8	0.00899	23.93	0.65	0.120
π C2-C4	1.66050	π* C6-C7	0.31603	35.31	0.50	0.119
π C6-C7	1.64051	π* C3-C5	0.30462	38.07	0.49	0.123
π C3-C5	1.64912	π* C2-C4	0.38205	40.61	0.48	0.125
π C2-C4	1.66050	π* C3-C5	0.30462	42.94	0.50	0.132
π C3-C5	1.64912	π* C6-C7	0.31603	45.00	0.49	0.134
π C6-C7	1.64051	π* C2-C4	0.38205	49.99	0.47	0.138
π* C2-C4	0.38205	π* C3-C5	0.30462	530.18	0.01	0.125
π* C2-C4	0.38205	π* C6-C7	0.31603	597.49	0.01	0.129

- [a]E(2) means energy of hyper conjugative interaction
- [b]Energy difference between donor and acceptor I and j NBO orbitals
- [c]F(I, j) is the Fock matrix element between i and j NBO analysis.

It is clear from above data, that the possible interactions with donors, acceptors and their electron densities of strong inter molecular interaction of Π electron with energy contribution from:

σ (N1-C8)   →   σ*(C2-C8) 11.34Kcal/mol, σ (C2-C8) → σ*(N1-C8) 13.20Kcal/mol,

π (C3-C5)   →   π* (C2-C4) 40.61Kcal/mol,   (C3-C5) →π* (C6-C7) 45Kcal/mol,

π (C6-C7) →   π* (C2-C4) 49.99Kcal/mol. The lone pair of interaction were prominent in the

compound as expected due to the charge transfer that take place from lone pair atoms in the ring.

The prominent interactions shower higher E2 values were * (C2-C4) →π* (C3-C5)

530.18Kcal/mol and π* C2-C4 →   π* (C6-C7) 597.49Kcal/mol.

8. Mulliken analysis

The total atomic charges of the molecule obtained by Mulliken using HF and B3LYP with basis set were listed in Table. 7 and the graphical representation of the atomic charges are shown in Fig. 6.

Mulliken charges arise from the Mulliken population analysis and provide a means of atomic charge distribution in the molecule from carried out computational methods. In the application of Quantum mechanical calculations to molecular system, the atomic charges calculations play in important role [21].

The nitrogen atom (N1) carries negative charge and carbon atom (C8) attached to nitrogen atom is carries positive charge due the electrons withdrawing nature of the nitrogen atom. Carbon atom (C2) present in the ring is carries negative charge and other carbon atoms in the ring also carry negative charge at DFT level. All hydrogen atoms present in the molecule have positive charge. The charge distribution on the molecule has an important influence on the vibrational spectra.
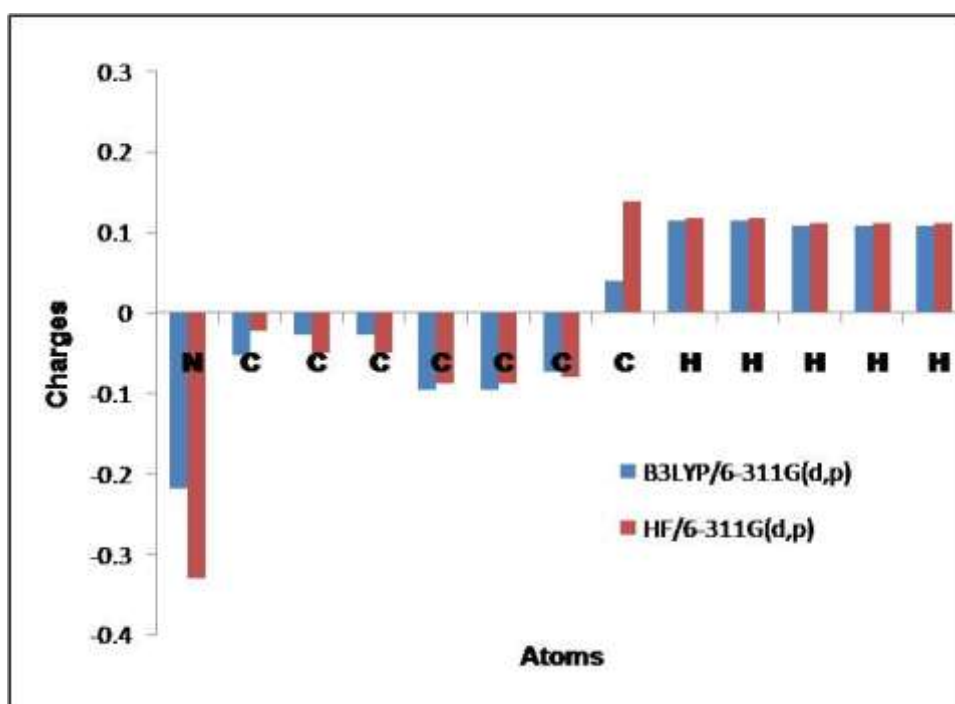

Fig. 6 Mulliken graph for Benzonitrile at B3LYP/6-311G(d, p) and HF/6-311G(d, p) level.

Table .7 Mulliken Population Analysis of Benzonitrile

ATOMS	B3LYP/6-311G(d,p)	HF/6-311G(d,p)
1 N	-0.218605	-0.329867
2 C	-0.052137	-0.022300
3 C	-0.027609	-0.049857
4 C	-0.027609	-0.049857
5 C	-0.095909	-0.088200
6 C	-0.095909	-0.088200
7 C	-0.073846	-0.080286
8 C	0.038884	0.138529
9 H	0.114089	0.117276
10 H	0.114089	0.117276
11 H	0.108192	0.111871
12 H	0.108192	0.111871
13 H	0.108180	0.111745

9. Thermodynamic Properties

On the basis of vibrational analysis at DFT/B3LYP/6-311G(d, p) and HF/6-311G(d, p) level, several thermodynamic parameters are calculated and are presented in Table. 8. All the thermodynamic properties are helpful information for further study of the title molecule. This can be used to compute the other thermodynamic energies according to relationship of thermodynamic functions and estimate direction of chemical reactions according to second law of thermo dynamical field [22]. The value of zero point vibrational energy (ZPVEs) in B3LYP/6-311G(d, p) is lower than HF/6-311G(d, p)method but the value of specific heat capacity(C) and entropy(S) are in B3LYP/6-311G(d, p) higher than HF/6- 311G(d, p) method. Dipole moment reflects the molecular charge distribution and is given as vector in three dimensions. Therefore, it can be used as descriptor to depict the charge movement across the molecule depends on the centre of positive and negative charges. The total dipole moment of Benzonitrile is calculated by B3LYP/6-311G(d, p) and HF/6-311G(d, p)methods are 4.5741 and 4.8352 Debye, respectively.

Table. 8 Thermodynamic parameters of Benzonitrile

Thermodynamic parameters	DFT-B3LYP/ 6-311G(d,p)	HF-B3LYP/ 6-311G(d,p)
SCF energy (a.u.)	-324.573245886	-322.507481979
Total energy (thermal)	65.921	69.907
Vibrational energy E_{vib}(kcal/mol)	64.143	68.129
Zero point Vibrational energy	62.09848	66.32606
Specific heat, C_V (cal/mol K)	23.171	21.421
Entropy, S (cal/mol K)	78.495	77.058
Rotational constant (GHz)		
X	0.889	5.75046
Y	2.981	1.56759
Z	27.798	1.23180
Dipole moment μ (Debye)		
μx	-4.5741	-4.8352
μy	0.0000	0.0000
μz	0.0001	0.0001
Total	4.5741	4.8352

10. Conclusion

Density functional calculations have been successfully performed for the title molecule Benzonitrile . The FT-IR and the FT-Raman spectrum of the molecule was recorded in the region 4000-400 cm^{-1} and 4000-100 cm^{-1} respectively. The observed and calculated frequencies are found to be in good agreement. The optimized geometries, harmonic frequencies were determined and analyzed both at HF and DFT/B3LYP levels of theories using 6-311G(d, p) basis sets. The theoretical results have been compared with experimental vibrations and values obtained from DFT/B3LYP/6-311G(d, p) level is in good agreement with the experimental values. NBO analysis shows that charge transfer takes place in the molecule. Thermodynamic parameters such as the zero point vibrational energy, entropy, heat capacity rotational constants have been computed out. Mulliken atomic charges have been calculated and properly tabulated and its graphical represented was also shown.

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