Spectroscopic Investigations, Computational Studies and Molecular Properties of Naphthalene Derivatives

OPEN ACCESS

Volume: 9

Special Issue: 1

Month: May

Year: 2022

P-ISSN: 2321-788X

E-ISSN: 2582-0397

Impact Factor: 3.025

Citation:
Mohandass, P., et al. "Spectroscopic Investigations, Computational Studies and Molecular Properties of Naphthalene Derivatives." *Shanlax International Journal of Arts, Science and Humanities*, vol. 9, no. S1, 2022, pp. 47–69.

DOI:
https://doi.org/10.34293/sijash.v9iS1-May.5944

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Abstract

Theoretical studies have been carried out on bio active molecules such as Naphthalene (npa) and its derivatives naphthalene-2-sulfonic acid (nsa) and 1-nitroso-2-naphthol (nnol) using both Ab initio HF and DFT-B3LYP methods with 6-311++G(d,2p) basis sets. The geometrical parameters, molecular properties and vibrational spectra of nsa, nnol and npa were calculated and analyzed. Geometrical optimizations of the nsa, nnol and npa molecules were done by Density Functional Theory (DFT) using the B3LYP function and Hartree-Fock (HF) level with 6-311++G(d,2p) basis set. The optimized molecular geometry and computed vibrational spectra are compared with experimental results which show significant agreement. DFT and HF global chemical reactivity descriptors (chemical hardness, total energy, electronic chemical otential and electrophilicity) are calculated for the title molecules and used to predict their relative stability and reactivity.

Keywords: DFT, HOMO – LUMO, IR, Naphthalene.

Introduction

Naphthalene and its derivatives were used as a precursor for various dyestuffs , pigments, resins, rubber processing chemicals, tanning agent and as wetting agent that effectively disperse colloidal systems in aqueous media [1]. Naphthalene and its derivatives are the most important class of organic compounds and are important products of industrial chemical processes. Naphthalene derivatives have good ability to form metal chelates and they are sensitive and specific reagent for fluorimetric determinations of tyrosine residues in proteins & peptides [2] and also show good cytotoxic action and anti-malarial potential [3,4]. To the best of our knowledge, very limited studies have been reported on DFT and HF global chemical reactivity descriptors of naphthalene derivatives (nsa and nnol). Therefore, the present study aims to give a complete description of the molecular geometry, molecular vibrations, HOMO-LUMO energies and global chemical reactivity descriptors of the titled molecule.

Materials and Methods

Experimental

The polycyclic aromatic compounds of Naphthalene (npa) and its derivatives naphthalene-2-sulfonic acid (nsa) and 1-nitroso-2-naphthol (nnol) were used for the spectral measurements. The FTIR spectrum was recorded by KBr pellet method on BRUKER-ALPHA-PLATINUM-ATR-IR6V spectrometer in the region 400-4000cm^{-1}.

Computational Method

Density functional theory (DFT) and Hartree-Fock (HF) calculations were performed with Gaussian-03 program using using the Becke-3Lee-Yang-Parr (B3LYP) functional supplemented with the standard 6-311++ G(d,2p) basis set [5,6]. The optimized structural parameters used in the vibrational wave number calculations at the HF and DFT levels to characterize all stationary points as minima. 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 wavenumber calculations. GaussView 3.07 program has been used to construct optimized molecular geometry, HOMO, LUMO energy distributions and HOMO–LUMO energy gap. The optimized geometry of the titled compounds and their molecular properties such as bond length, bond angle, dipole moment and several global descriptors have been used to understand their structural properties and chemical reactivities.

Results and Discussion

Molecular Geometry

The optimized structure parameters of all three compounds (npa, nsa and nnol) using DFT/B3LYP and HF levels with the 6-311++ G(d,2p) basis set are listed in Table 1 and 2. The optimized geometries of Naphthalene (npa) and its derivatives (naphthalene-2-sulfonic acid (nsa) and 1-nitroso-2-naphthol (nnol) are shown in Figure 1.

The bond angle, bond length and dihedral angle of Naphthalene (npa) and its derivatives (naphthalene-2-sulfonic acid (nsa) and 1-nitroso-2-naphthol (nnol) are listed in Table 3-8. The total energies of npa, nsa and nnol at DFT/B3LYP level with the basis set 6-311++G(d,2p) are found to be -385.9921, -1171.6621 and -590.5592 a.u. with dipole moments 0.0, 7.0975 and 6.102 Debye respectively whereas the total energies of npa, nsa and nnol at HF level with the basis set 6-311++G(d,2p) are found to be -383.4408, -1166.8963 and -586.9892 a.u. with dipole moments 0.0, 7.4279 and 5.5827 Debye respectively. Dipole moment of nsa is greater than that of nnol. This is due to increase in size of sulfonic acid group. This compound has C-C, C-H, O-H, C-O, S-O, S=O, C-S, N=O, N-C and C-N bonds. All C-C bond lengths in benzene ring are around 1.35 - 1.43 A^0. Almost all carbon-hydrogen (C-H) bond distance are nearly equal to 1.08 A^0 and carbon-carbon bond distance are approximately equal to 1.38-1.42 A^0. It is interesting to note that the O-H bond length is the range 0.93-0.96 A^0 in nnol compared to standard bond length 0.98 A^0. In DFT method the N=O bond length is equal to 1.216 A^0 compared to standard bond length 1.21 A^0. But in HF method, this is lower (1.173 A^0) than the standard bond length. In DFT method the S=O bond length is equal to 1.51 A^0 (1.47 A^0 in HF method) compared to standard bond length 1.43 A^0. In the substituted naphthalene, the ring carbon atoms exert a large attraction on the valence electron cloud of the H atom resulting in an increase in the C-H force constant and a decrease in the corresponding bond length. All C-C-C bond angles in phenyl ring are around 118 - 120^0. The bond angle of 3C-4C-5N is 119.01^0 whereas the bond angle of C11-C4-C3 is 119.11^0 in all three compounds. The presence of substituents in naphthalene ring does not alter the bond angle values. The dihedral angles of most of the bonds are equal to 180^0 and the presence of substituent in the naphthalene ring does not affect the dihedral angle values.

Mulliken Atomic Charge

The Mulliken atomic charges distribution of Naphthalene (npa) and its derivatives (naphthalene-2-sulfonic acid (nsa) and 1-nitroso-2-naphthol (nnol) are shown in Fig. 2 and the values are given in Table 6. The Mulliken charges are charges based in the local electron density (charge density) and it's depending strongly of the basic set and the functional, because it is sensitive to the probability density. Oxygen atom has a maximum negative charge and the atomic charge of oxygen atom (-0.426) in sulfonic acid is greater than that of oxygen atom (-0.057) in phenolic OH group. Further, the atomic charge of oxygen atom has positive value (0.038) in nitroso group in 1-nitroso-2-naphthol. The atomic charge of nitrogen aton in nnol has negative value (-0.22) whereas the atomic charge of sulfur atom atom has highest positive value (0.833). Except C3 and C4, all other carbon atoms have negative charge because C3 and C4 carbon atoms fusing the benzene ring. However, all the hydrogen atoms exhibit a net positive charge (range 0.136 – 0.208) in 6-311++G(d,2p) basis set but the H11 have high value (≈0.249).

Vibrational Assignments

Vibrational spectroscopy is a valuable tool for the elucidation of molecular structure. The experimental and theoretical IR spectra of Naphthalene (npa) and its derivatives (naphthalene-2-sulfonic acid (nsa) and 1-nitroso-2-naphthol (nnol) are shown in Figures 3-5. Using Gauss View 5.0 molecular visualization program, the vibrational frequency assignments and other parameters were made. All calculations were done for optimized structure in gas phase. On the basis of the comparison between calculated and experimental results, assignments of fundamental modes were examined. The calculated frequencies are slightly higher than the observed values for the majority of the normal modes. Two factors may be responsible for the discrepancies between the experimental and computed spectra of this compound. The first is caused by the environment and the second reason for these discrepancies is the fact that the experimental value is an anharmonic frequency while the calculated value is a harmonic frequency. The vibrational modes of experimental and theoretical values were assigned and listed in Table 7-9. A linearity between the experimental and calculated wave numbers for the Naphthalene (npa) and its derivatives (i.e. for the whole spectral range considered), can be estimated by plotting the calculated versus experimental wave numbers and shown in Fig. 6-8.

In the title compounds, aromatic C-H stretching vibration is observed around 3000-3190 cm-1 and the assignment correlate with theoretical calculated value (3180-3200 cm^{-1} in DFT and 3330-3350 in HF). The α,α' C-H bending is observed at 1123 cm^{-1} and the assignment correlate with theoretical calculated value (1390 cm^{-1} in DFT and 1173 in HF). The calculated O-H stretching frequency (DFT) in i-nitroso-2-naphthol was obtained at 824 cm^{-1} (4235 in HF method) and the corresponding experimental peak was observed at 3650 cm^{-1}. The experimental C=C stretching frequency (1737 cm^{-1}) is associated with theoretical value (1767 cm^{-1} in DFT and 1764 in HF). In naphthalene (nap), C-H bending vibration is observed around 1554 cm^{-1} and the assignment correlate with theoretical calculated value (1546 cm^{-1} in DFT and 1526 in HF). The experimental symmetric S=O stretching vibration (644 cm^{-1}) is closely associated with theoretical value (635 cm^{-1} in DFT and 639 in HF). The calculated asymmetric S=O stretching vibration was obtained at 1046 cm^{-1} in DFT method (1023 in HF) and the corresponding experimental value was observed at 1049 cm^{-1}. The calculated S-O stretching vibrations (930, 941 in DFT and 903,926 in HF) of the sulfonic acid group was coupled with skeletal modes were observes in the region 945 - 975 cm^{-1}. The experimental N=O bending vibrations (765 cm^{-1}) are very close to theoretical values 770 cm^{-1} in DFT method (751 in HF). Further, the experimental N=O stretching primary vibrations (1620 cm^{-1}) are very close to theoretical values 1667 cm^{-1} in DFT method (1668 in HF).

The experimental O-H bending frequency was obtained at 1250 cm^{-1} and the theoretical peaks were observed at 1285 cm^{-1} in DFT method (1206 in HF).

Frontier Molecular Orbitals

Frontier molecular orbital are the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) and play an important role in optical and electrical properties, and UV-VIS spectra. The energy gap between HOMO and LUMO determines the kinetic stability, chemical reactivity and optical polarizability and chemical hardness– softness of a molecule [7,8]. The HOMO energies, the LUMO energies and the energy gap for Naphthalene (npa) and its derivatives (naphthalene-2-sulfonic acid (nsa) and 1-nitroso-2-naphthol (nnol) molecules have been calculated using B3LYP level with 6-311++G (d,2p) basis set. The HOMO-LUMO energy gap of Naphthalene (npa) and its derivatives (naphthalene-2-sulfonic acid (nsa) and 1-nitroso-2-naphthol (nnol) was calculated at the DFT (B3LYP)/6-31++G (d,2p) level reveals that the energy gap reflects the chemical activity of the molecules.

The calculated energy value of HOMO of naphthalene is -0.2262 eV and LUMO is -0.0518 eV in gaseous phase in DFT method. The value of energy separation between the HOMO and LUMO is 0.1744 eV explains the eventual charge transfer interaction within the molecule, which influences the biological activity of the molecule. Similarly, the calculated energy value of HOMO is -0.2944 eV and LUMO is 0.0385 eV in gaseous phase and the energy separation between the HOMO and LUMO is 0.3329 in HF method. Similarly, the energy gap for naphthalene-2-sulfonic acid (nsa) molecule is -0.1635 in DFT (-0.2833 in HF) method and the energy gap for 1-nitroso-2-naphthol (nnol) molecule is -0.11 in DFT (-0.3348 in HF) method The lowering of HOMO and LUMO energy gap supports the bioactivity of the molecule. The 3D plots of HOMO and LUMO are shown in Figures 9 and 10.

The contoun map and molecular electrostatic potential (MEP) map Naphthalene (npa) and its derivatives (naphthalene-2-sulfonic acid (nsa) and 1-nitroso-2-naphthol (nnol) is shown in the Fig.11 and 12. It is useful to study the electrophile attracted negative regions (where the electron distribution effect is dominant). In the majority of the MEP, while the maximum negative region which preferred site for electrophilic attack indications as red colour, the maximum positive region which preferred site for nucleophilic attack symptoms as blue colour. The MEP diagram is very useful in research of molecular structure with its physiochemical property relationship [9].

Global Chemical Reactivity Descriptors

Density Functional Theory (DFT) has been employed for the calculation of molecular properties and to provide qualitative explanation for several findings in many areas of chemistry and biology [10,11]. Global chemical reactivity descriptors of compounds such as electronegativity (χ), chemical potential (μ), hardness (η), softness (S) and electrophilicity index (ω) are deduced from ionization potential and electron affinity values. Softness (S) is a property of compound that measures the extent of chemical reactivity. It is the reciprocal of hardness [12]. The ionization energy (IE) can be expressed through HOMO orbital energies as IE=-εHOMO and electron affinity (EA) can be expressed through LUMO orbital energies as EA= -εLUMO, which are also reported in the same table.

By using HOMO and LUMO energy values for a molecule, chemical potential, electro negativity and chemical hardness can be calculated [13]. All calculations were performed using the Gaussian 03 package [14]. The above expression s used as working equations to calculate the group electro negativity, group hardness, softness and other properties. The values of ionization potential, electronegativity, hardness (η), softness (ζ) and electrophilicity index (ω) that are obtained [15,16] for the titled molecules are listed in Tables 10-11. A good reactive electrophile is characterized by higher value of ω, and conversely a more reactive nucleophile is characterized by a lower value of ω. The global reactivity descriptors such as ionization potential (I), electron affinity (A), chemical hardness (η), chemical softness (S), chemical potential (μ) an electrophilicity index (ω) values were examined with DFT / B3LYP / 6-311G(d,2p) level to have information about the chemical reactivity and relative stability of the titled molecules. A linear relationship between electron affinity (A) and electrophilicity (ω) of titled molecules was observed. Substituted naphthalene possesses the lower softness values.

Conclusions

In this work, The optimized structures and parameters of Naphthalene (npa) and its derivatives (naphthalene-2-sulfonic acid (nsa) and 1-nitroso-2-naphthol (nnol) calculated by DFT/B3LYP levels with the 6-311++G(d,2p) basis set are studied. A complete vibrational analysis of muf are by performed HF and DFT-B3LYP methods with 6-311++G(d,2p) basis sets. The influences of substitutions of –OH, NO and SO3H with ring are investigated and the vibrational frequencies of the title compounds are discussed. The observed and stimulated spectra are agreed for the good frequency fit in DFT B3LYP/6-311++G(d,2p) method. The less standard deviation between theoretical and experimental wave numbers is confirmed by the qualitative agreement between the calculated and observed frequencies and various parameters like bond lengths, bond angles and dihedral angles are also calculated by both DFT and HF methods. Global descriptors such as frontier orbital gap (ΔE), electrophilicity (ω), softness (S) and ionization energy (I) were determined and applied to identify the differences in the reactivity of titled molecules.The value of energy separation between the HOMO and LUMO of all three compounds explains the eventual charge transfer interaction within the molecule, which influences the biological activity of the molecule. The lowering of HOMO and LUMO energy gap supports the bioactivity of the molecule. The reactivity indices calculated by DFT method have been successfully applied to the concept of chemical reactivity.

References

1. Gerd Collin, HartmutHöke , Helmut Greim “Naphthalene and Hydronaphthalene “in Ullmann’s Encyclopedia of Industrial Chemistry Wiley-VCH, Weinheim , (2003)
2. InnocentBenjamin, Akaninyene D.Udoikono, HitlerLouis, Ernest C.Agwamba, Tomsmith O.Unimuke, Aniekan E.Owen, Adedapo S.Adeyinka, J. Mol Struc., 1264 (2022) 133298
3. F. Sundler, L.J. Larsson and R. Hakanson., Histochemistry, 50 (1976) 39.
4. M.P.M. Poztela, S.H.F. Villamil, L.J. Perissinotti and A.O.M. Stoppani., Biochem. Pharmacol, 52, (1996) 1875.
5. A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
6. C. Lee, W. Yang, R.G. Parr, Phys. Rev. BB7 (1998) 785.
7. Senyel, M.; Alver, Ö.;Parlak, C. Spectrochim. ActaA., 71 (2008) 830.
8. Parlak, C.; Alver, Ö.;Senyel, M.; Spectrochim. ActaA., 69 (2008) 1252.
9. A. Suvitha, S. Periandy, S. Boomadevi, M. Govindaraja,. Spectrochimica Acta Part A: Molecular and Biomolecular spectroscopy 117 (2014) 216–224.
10. Kohn, W.; Becke, A.D.; Parr, R.G.J Phys chem. 1996, 100, 12974.
11. Geerlings, P.; De Proft, F.; Langenaeker, W. chem Rev 2003, 103, 1793.
12. Renuga S, Karthikesan M, Muthu S (2014), Spectrochim Acta Part A 127: 2014, 439-453.
13. Pearson RG (1986) Absolute electro negativity and hardness correlated with molecular orbital theory.Proc Natl Acad Sci 83(22):8440-8441

14. Fisch MJ, Trucks GW, Schlegel HB,Scuseria GE, Robb MA,Cheeseman JR, Montgomery JA jr,Vreven T, Kudin KN,Burant JC, Millam JM, lyengar SS, tomasi J, Barone V,Mennucci B, Cossi M, Scalmani G,Rega N,Petersson GA, Nakatsuji H, Hada M,Ehara M, Tcyota K, Ukuda R,Hasegawa J, lshida M,Nakajima T,Honda Y, Kitao OO, Nakai H, Klene M, Li X, Knox JE, Hratchian HP,Cross JB,Adamo C,Jaramillo J,Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R,Pomelli C,Ochterski JW, Ayala PY,Morokuma K,Voth GA, Salvador P,Dannenberg JJ,Zakrzewski VG,Dapprich S,Daniels AD,Strain MC,Farkas O, Malick DK,Rabuck AD, Raghavachari K,Foresman JB, Ortiz JV, Cui Q,Baboul AG, Clifford S, Ciosiowski J, Stefanov BB,Liu G, Liashenko A, Piskorz P, Komaromi L,Martin RL, Fox DJ,Keith T, Al –Laham MA,Peng CY,Anayakkara A, Challacombe M,Gill PMW, Johnson B,Chen W,Wong MW, Gonzalez C, Pople JA(2009)Gaussian 09, Revision A02.Gaussian lnc, Wallingford CT.
15. Chattaraj, p.k and Giri, S., Jouranal of physical chemistry A,111, (2007) 11116-11121.
16. Padmanabhan, J.,Parthasarathi, R., Subramanian , V and chattaraj , p. k journal of physical chemistry A, 111,(2007) 1358-1361.

Table 1 Optimized Structure Parameters of Naphthalene (nap), Naphthalene-2-sulfonic acid (nsa) and 1-nitroso-2-naphthol (nnol) by DFT method

File Name	**Naphthalene (nap)**	**Naphthalene-2-sulfonic acid (nsa)**	**1-nitroso-2-naphthol (nnol)**
File Type	nap .chk	nsa.chk	nnol.chk
Calculation Type	FREQ	FREQ	FREQ
Calculation Method	RB3LYP	RB3LYP	RB3LYP
Basis Set	6-311++G(D,2P)	6.311++G(D,2P)	6-311++G(D,2P)
Charge	0	0	0
Spin	Singlet	singlet	Singlet
Total Energy	-385.99211201	-1171.66211931	-590.55921157
Dipole moment	0.0000Debye	7.0975	6.1020Debye

Table 2 Optimized Structure Parameters of Naphthalene (nap), Naphthalene-2-sulfonic acid (nsa) and 1-nitroso-2-naphthol (nnol) by HF method

File Name	**Naphthalene (nap)**	**Naphthalene-2-sulfonic acid (nsa)**	**1-nitroso-2-naphthol (nnol)**
File Type	.chk	NSA.chk	nnol.chk
Calculation Type	FREQ	FREQ	FREQ
Calculation Method	RHF	RHF	RHF
Basis Set	6-311++G(D,2P)	6-311++G(D,2P)	6-311++G(D,2P)
Charge	0	0	0
Spin	Singlet	singlet	Singlet
Total Energy	-383.44088332	-1166.89633583	-586.98923133
Dipole moment	0.0000Debye	7.4279	5.5827Debye

Table 3 a) Bond distances of Naphthalene (nap)

Bond	Bond Distance-DFT	Bond Distance-HF
C2-C1	1.3744983	1.3584115
C3-C2	1.4201009	1.4203429
C4-C3	1.4313369	1.4081421
C5-C4	1.4201147	1.4203433
C6-C5	1.3744924	1.3584113
H7-C10	2.161051	2.1553599
H8-C1	1.08182	1.0732698
H9-C2	1.0827912	1.07396
C10-C3	1.4201186	1.4203767
C11-C4	1.4201076	1.4203761
H12-C5	1.0827938	1.0739606
H13-C6	1.0818203	1.0732695
C14-C11	1.3744941	1.3583869
C15-C10	1.3744908	1.3583874
H16-C11	1.0827891	1.0739594
H17-C14	1.0818217	1.0732703
H18-C15	1.0818203	1.073269

b) Bond distances of Naphthalene-2-sulfonic acid (nsa)

Bond	Bond Distance-DFT	Bond Distance-HF
C2-C1	1.3752955	1.359456
C3-C2	1.4186455	1.4186339
C4-C3	1.4302015	1.4060824
C5-C4	1.4193237	1.4188064
C6-C5	1.3748077	1.3590838
H7-C3	2.1630091	2.1579218
H8-C1	1.0818998	1.0733067
H9-C2	1.0827447	1.0737484
C10-C3	1.4214236	1.4225515
C11-C4	1.4198012	1.4211751
H12-C5	1.0823757	1.0735299
H13-C6	1.081736	1.0730322
C14-C11	1.3712062	1.354762
C15-C10	1.3715186	1.354657
H16-C11	1.081097	1.0715351
H17-C15	1.0802625	1.0712512
S18-C14	1.80174	1.7725904
O19-S18	1.5134162	1.4707036
O20-S18	1.4639602	1.4277909

O21-S18	1.5141056	1.4713508
Na22-O20	2.225517	2.2266759

c) Bond distances of 1-nitroso-2-naphthol (nnol)

Bond	Bond Distance-DFT	Bond Distance-HF
C2-C1	1.4004896	1.3764604
C3-C2	1.4338594	1.4329837
C4-C3	1.4313818	1.4091953
C5-C4	1.4221741	1.4197794
C6-C5	1.3645828	1.3510374
H7-C3	2.1860649	2.1804152
C8-C3	1.4201019	1.4221707
C9-C4	1.4178469	1.4197184
H10-C5	1.0812457	1.0720768
H11-C6	1.0814263	1.0723373
C12-C9	1.3746469	1.3573369
C13-C8	1.3750091	1.3578756
H14-C9	1.0821241	1.0731131
H15-C12	1.0815206	1.0729782
H16-C13	1.0810932	1.0724747
N17-C1	1.4299793	1.4287426
O18-N17	1.2165742	1.173071
O19-C2	1.3451197	1.329959
H20-O19	0.9619918	0.9369029

Table 4 a) Bond angles of Naphthalene (nap)

Bond	Bond Angle(°)-DFT	Bond Angle(°)- HF
C3-C2-C1	120.8621783	120.7530335
C4-C3-C2	118.8528859	118.9985167
C5-C4-C3	118.8503778	118.99839
C6-C5-C4	120.8628431	120.7530955
H7-C3-C2	96.248461	96.1419729
H8-C1-C2	120.0969504	120.1924117
H9-C2-C1	120.3500749	120.3391032
C10-C3-C2	122.2967149	122.0033714
C11-C4-C3	118.8533623	118.997986
H12-C5-C4	118.7874486	118.9078061
H13-C6-C5	120.0973239	120.1925507
C14-C11-C4	120.8613829	120.7533076
C15-C10-C3	120.8622014	120.7533124
H16-C11-C4	118.7873012	118.9067312

H17-C14-C11	120.0979681	120.1932817
H18-C15-C10	120.0970788	120.1936621

b) Bond angles of Naphthalene-2-sulfonic acid (nsa)

Bond	Bond Angle(°)-DFT	Bond Angle(°)- HF
C3-C2-C1	120.758573	120.60861
C4-C3-C2	118.8515262	118.97481
C5-C4-C3	119.0189209	119.23832
C6-C5-C4	120.7227259	120.61258
H7-C3-C2	96.3527641	96.290989
H8-C1-C2	120.0279991	120.09813
H9-C2-C1	120.3592844	120.3809
C10-C3-C2	122.3504237	122.08693
C11-C4-C3	119.1098453	119.21487
H12-C5-C4	118.776558	118.8943
C13-C6-C5	120.1039292	120.2531
C14-C11-C4	120.1432451	120.25141
C15-C10-C3	121.0333995	120.85662
H16-C11-C4	120.1807423	119.82471
H17-C15-C10	120.55544	120.46741
S18-C14-C11	118.8844309	119.2186
O19-S18-C14	106.2017876	106.52795
O20-S18-C14	106.5343646	106.9705
O21-S18-C14	107.1185657	107.22308
Na22-O20-S18	92.8861267	94.319325

c) Bond angles of 1-nitroso-2-naphthol (nnol)

Bond	Bond Angle(°)-DFT	Bond Angle(°)- HF
C3-C2-C1	119.5636798	119.2724687
C4-C3-C2	119.0711747	119.2089849
C5-C4-C3	119.8485935	120.0729117
C6-C5-C4	119.9045117	119.4931655
H7-C3-C2	97.1857906	97.3214394
C8-C3-C2	122.3245044	122.2341372
C9-C4-C3	118.6604002	118.9040327
H10-C5-C4	119.1417619	119.4455298
H11-C6-C5	121.8403251	121.346286
C12-C9-C4	121.2752061	121.1275999
C13-C8-C3	121.2475672	121.2199926
H14-C9-C4	118.4132798	118.4780788
H15-C12-C9	120.1585008	120.2460676

H16-C13-C8	119.9817914	120.0615539
N17-C1-C2	127.3667565	126.9967818
O18-N17-C1	117.8302262	118.3482111
O19-C2-C1	119.1821214	119.7623131

Table 5 a) Dihedral angles of Naphthalene (nap)

Bond	Dihedral Angle(°) DFT	Dihedral Angle(°)-HF
H7-C3-C2-C1	-180	-179.9993887
H8-C1-C2-C3	-180	179.9994686
H9-C2-C1-C6	180	-180
C10-C3-C2-C1	179.9997295	-179.9994897
C11-C4-C3-C2	180	179.9994736
H12-C5-C4-C3	179.9995692	-180
H13-C6-C5-C4	180	-180
C15-C10-C3-C2	-179.9996855	-179.9995025
H16-C11-C4-C3	179.9996043	179.9996165
H17-C14-C11-C4	-179.9995142	180
H18-C15-C10-C3	180	180

b) Dihedral angles of Naphthalene-2-sulfonic acid (nsa)

Bond	Dihedral Angle (°)	Dihedral Angle (°)-HF
H7-C3-C2-C1	-179.709067	-179.5545324
H8-C1-C2-C3	-179.9797735	-179.9651327
H9-C2-C1-C6	-179.9343607	-179.9264327
C10-C3-C2-C1	-179.8422209	-179.7875601
C11-C4-C3-C2	-179.9359555	-179.9637705
H12-C5-C4-C3	-179.9429998	-179.910396
H13-C6-C5-C4	179.9802571	179.9609729
C15-C10-C3-C2	179.9914465	179.9964403
H16-C11-C4-C3	179.5082734	179.3906122
H17-C15-C10-C3	-178.9563333	-178.5869954
S18-C14-C11-C4	-178.8880995	-177.8106138
O19-S18-C14-C11	-134.1618347	-140.8808654
O20-S18-C14-C11	112.5299526	105.8202638

c) Dihedral angles of 1-nitroso-2-naphthol (nnol)

Bond	Dihedral Angle-DFT	Dihedral Angle-HF
H7-C3-C2-C1	-179.9992795	-179.9988563
C8-C3-C2-C1	-179.9994483	-179.9990999
C9-C4-C3-C2	180	180
H10-C5-C4-C3	180	-180

H11-C6-C5-C4	-179.9995977	-179.9996797
C13-C8-C3-C2	-180	-180
H14-C9-C4-C3	-180	-179.9997241
H15-C12-C9-C4	-180	-180
H16-C13-C8-C3	-180	-180
N17-C1-C2-C3	179.9993064	179.9995347
O19-C2-C1-C6	-180	-180
H20-O19-C2-C1	-179.9995898	-179.997275

Table 6 a) The calculated Mulliken atomic charge distribution of Naphthalene (nap)

Atom	Atomic charge-DFT	Atomic charge-HF
C1	-0.250	-0.241
C2	-0.056	-0.087
C3	0.029	0.106
C4	-0.029	0.106
C5	-0.056	-0.087
C6	-0.250	-0.241
H7	0.136	0.112
H8	0.184	0.163
H9	0.136	0.112
C10	-0.056	-0.087
C11	-0.056	-0.087
H12	0.136	0.112
H13	0.184	0.163
C14	-0.250	-0.241
C15	-0.250	-0.241
H16	0.136	0.112
H17	0.184	0.163
H18	0.184	0.163

b) The calculated Mulliken atomic charge distribution of Naphthalene-2-sulfonic acid (nsa)

Atom	Atomic charge-DFT	Atomic charge-HF
C1	-0.189	-0.290
C2	-0.196	-0.061
C3	0.114	-0.048
C4	0.065	0.399
C5	-0.056	-0.087
	-0.164	0.094
C6	-0.241	-0.321
H7	0.153	0.127
H8	0.188	0.165

H9	0.131	0.109
C10	-0.325	-0.375
C11	-0.025	0.109
H12	0.143	0.114
H13	O.191	0.170
C14	-0.446	-1.018
C15	-0.265	-0.290
H16	0.206	0.202
H17	0.128	0.137
S18	0.833	1.323
O19	-0.426	-0.569
O20	-0.339	-0.473
021	-0.204	-0.304
Na22	0.668	0.800

c) The calculated Mulliken atomic charge distribution of 1-nitroso-2-naphthol (nnol)

ATOM	Atomic charge-DFT	Atomic charge-HF
C1	-0.225	-0.294
C2	-0.637	-0.582
C3	0.733	0.993
C4	0.179	0.338
C5	-0.139	-0.328
C6	-0.085	0.002
H7	0.089	0.065
C8	-0.230	-0.205
C9	-0.146	-0.103
H10	0.144	0.113
H11	0.249	0.242
C12	-0.279	-0.342
C13	-0.138	-0.228
H14	0.159	0.141
H15	0.190	0.166
H16	0.199	0.175
N17	-0.233	-0.263
O18	0.038	0.080
O19	-0.057	-0.181
H20	0.189	0.212

Table 7 Vibrational assignments of fundamental frequencies of naphthalene (npa) by DFT and HF methods

Sl. No.	Assignments	Experimental value (cm^{-1})	Theoretical value (cm^{-1}) 6.311(++)d,2p basis set-DFT method	Theoretical value (cm^{-1}) 6.311(++)d,2p basis set-HF method
1	Ar-Sym C-H stretching	3096	3185	3340
2	Sym C=C stretching	1844	1910	1822
3	Sym C=C stretching	1737	1767	1764
4	Out of plane C-H bending	1554	1546	1526
5	In-plane C-H bending	1310	1398	1360
6	Out of plane C-H bending	1274	1350	1273
7	α,α’ C-H bending	1123	1390	1173
8	Asym C-H stretching	1003	1034	1017
9	Out of plane C-H bending	846	951	855
10	Asym C-C stretching	618	653	670

Table 8 Vibrational assignments of fundamental frequencies of naphthalene-2-sulfonic acid sodium salt (nsa) by DFT and HF methods

Sl. No.	Assignments	Experimental value (cm^{-1})	Theoretical value (cm^{-1}) 6.311(++)d,2p basis set-DFT method	Theoretical value (cm^{-1}) 6.311(++)d,2p basis set-HF method
	Ar C-H stretching	3110	3173	3330
1	Sym C=C stretching	1622	1632	1612
2	Sym S=O stretching	1238	1225	1366
3	Sym S-O and S=O stretching	948,974	930,941	903, 926
4.	C-H stretching	864	857	834
5.	In plane C-H bending	825	818	834
6	Asym C-H stretching	769	778	709

7	Sym C-S stretching	684	669	633
8	Sym. S=O stretching	644	635	639
9	Sym S-O stretching	569	553	544
10	Asym S=O stretching	1049	1046	1023
11	Sym C=C stretching	1502	1540	1578
12	In-plane C-H bending	1269	1286	1246

Table 9 Vibrational assignments of fundamental frequencies of 1-nitroso-2-naphthol (nnol) by DFT and HF methods

Sl. No.	Assignments	Experimental value (cm^{-1})	Theoretical value (cm^{-1}) 6.311(++)d,2p basis set-DFT method	Theoretical value (cm^{-1}) 6.311(++)d,2p basis set-HF method
1	C=C stretching	651	638	630
2	C-O stretching	719	702	739
3	N=O bending	765	770	751
4	C=C bending	786	779	765
5	C-H bending	820	897	861
6	C-H bending	960	965	955
7	C=C stretching	1031	1053	1009
8	Out of plane C-H stretching	1120	1108	1174
9	O-H bending,	1250	1285	1206
10	C-H bending	1310	1309	1318
11	In plane C-H stretching	1468	1481	1408
12	N=O stretching	1620	1667	1668
13	Ar C-H stretching	3150	3179	3335
14	O-H stretching	3650	3824	4235

Table 10 Comparison of HOMO and LUMO energy gaps and other molecular Properties by DFT methods

Sl.No.	Properties	naphthalene (npa)	naphthalene-2-sulfonic acid (nsa)	1-nitroso-2-naphthol (nnol)
1	HOMO (eV)	-0.2262	-0.2276	-0.2154
2	LUMO (Ev)	-0.0518	-0.0641	-0.1054

3	HOMO-LUMO(ENERGY GAP)	-0.1744	-0.1635	-0.11
4.	ABSOLUTE HARDNESS	0.2003	0.19555	0.1627
5.	IONIZATION ENERGY	0.2262	0.2276	0.2154
6	ELECTRON AFFINITY	0.0518	0.0641	0.1054
7	ELECTRONEGATIVITY (I+EA)/2	0.139	0.14585	0.1604
8	CHEM POTENTIAL	-0.139	-0.14585	-0.1604
9	GLOBAL SOFTNESS	-3.5971	-3.4282	-3.1172
10	GLOBAL ELECTROPHILICITY	0.0482	0.0544	0.0791

Table 11 Comparison of HOMO and LUMO energy gaps and other molecular Properties by HF methods

Sl.No.	Properties	naphthalene (npa)	naphthalene-2-sulfonic acid (nsa)	1-nitroso-2-naphthol (nnol)
1	HOMO (eV)	-0.2944	-0.2973	-0.3049
2	LUMO (Ev)	0.0385	-0.014	0.0299
3	HOMO-LUMO(ENERGY GAP)	-0.3329	-0.2833	-0.3348
4.	ABSOLUTE HARDNESS	0.16645	0.14165	0.1674
5.	IONIZATION ENERGY	0.2944	0.2973	0.3049
6	ELECTRON AFFINITY	-0.0385	0.014	-0.0299
7	ELECTRONEGATIVITY (I+EA)/2	0.12795	0.15565	0.1375
8	CHEM POTENTIAL	-0.12795	-0.15565	-0.1375
9	GLOBAL SOFTNESS	-3.9078	-3.2123	-3.6364
10	GLOBAL ELECTROPHILICITY	0.0492	0.0855	0.0565

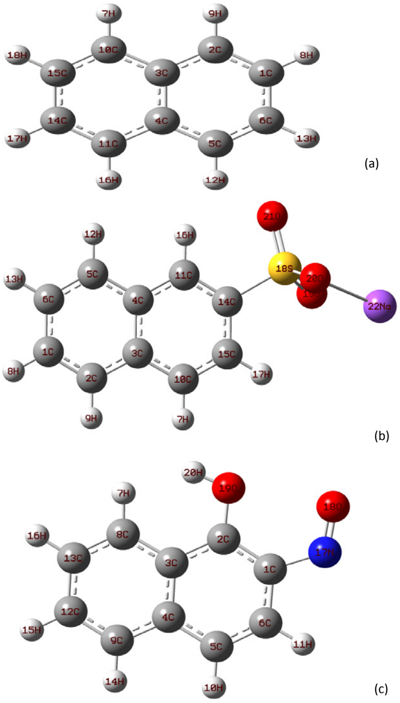
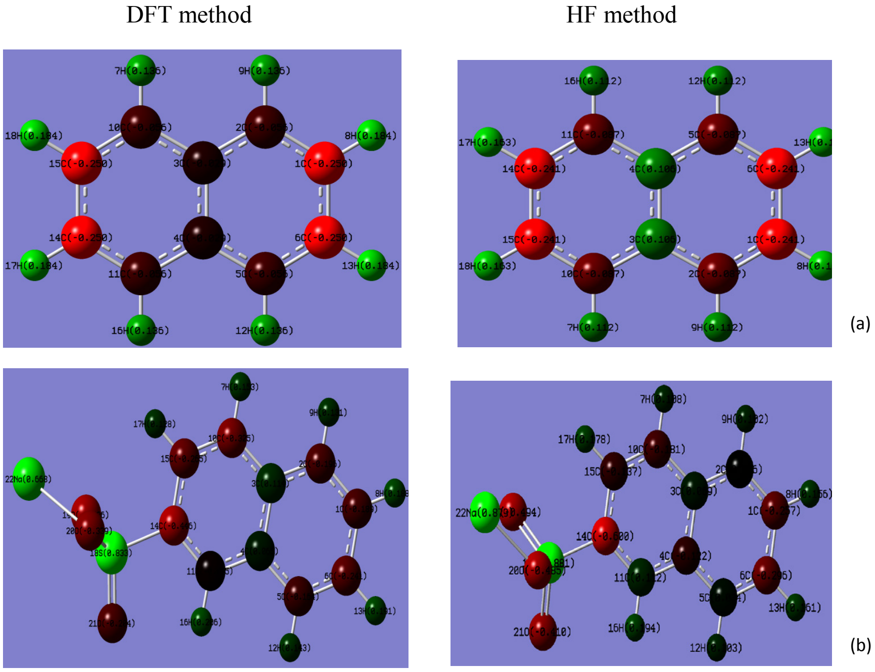


Figure 1 Optimized geometry of (a) Naphthalene (nap) (b) sodium salt of Naphthalene -2-sulfonic acid (nsa) and (c) 1-nitroso-2-naphthol (nnol) at B3LYP/6.311++G(d,2p) level


DFT method HF method

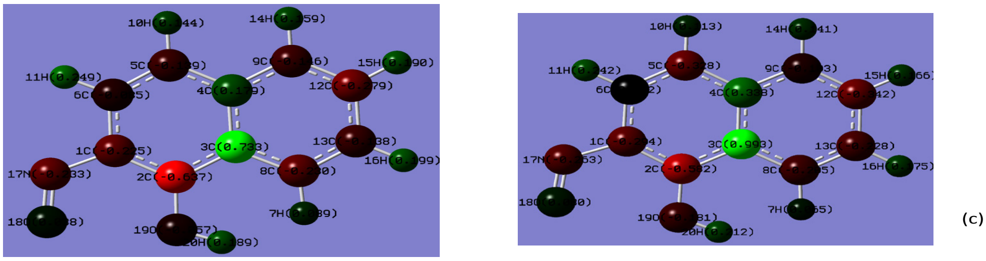


Figure 2 The Mulliken atomic charge distribution of (a) Naphthalene (nap) (b) sodium salt of Naphthalene -2-sulfonic acid (nsa) and (c) 1-nitroso-2-naphthol (nnol) at B3LYP/6.311++ G(d,2p) level by DFT and HF methods

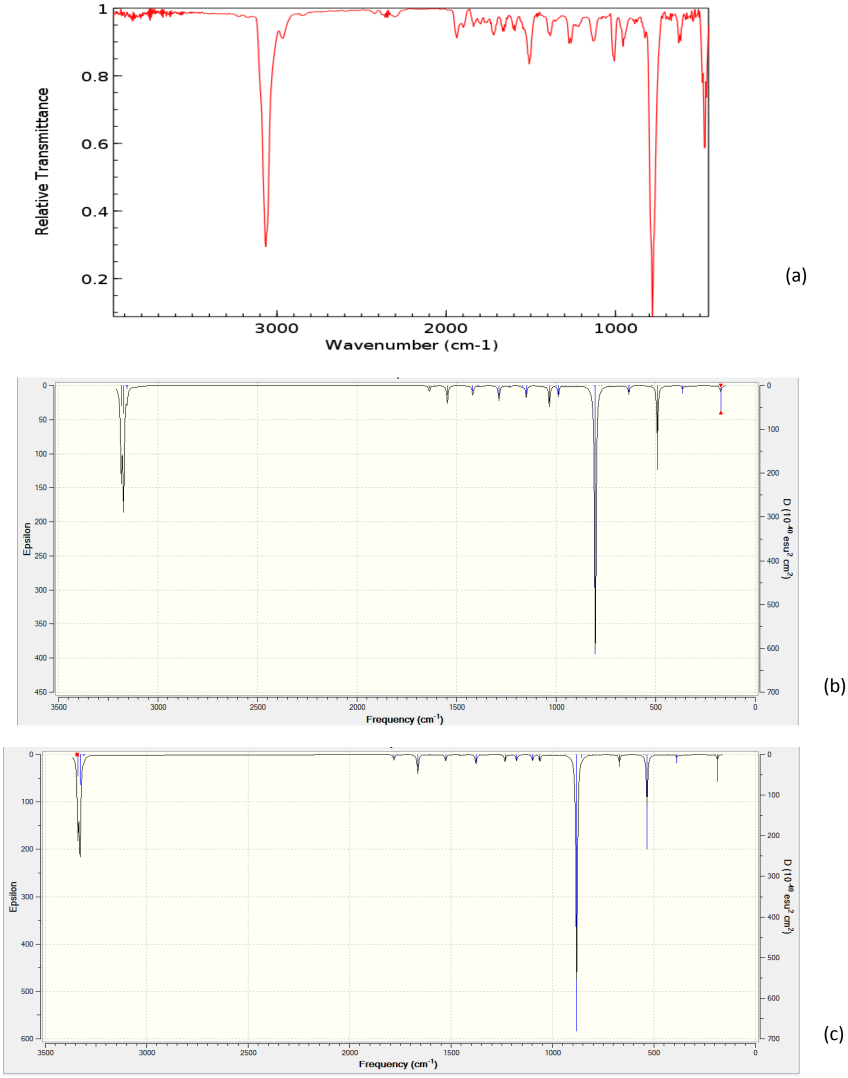
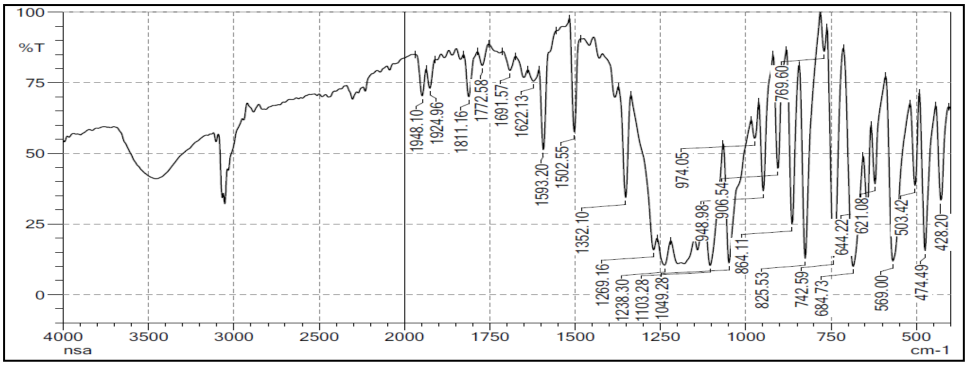


Figure 3 Experimental FT IR Spectrum (a) Normalized IR intensities of b) DFT method c) HF method for Naphthalene at B3LYP/ 6-311++G (d.2p) level



DFT method c) HF method for Naphthalene at B3LYP/ 6-311++G (d.2p) level

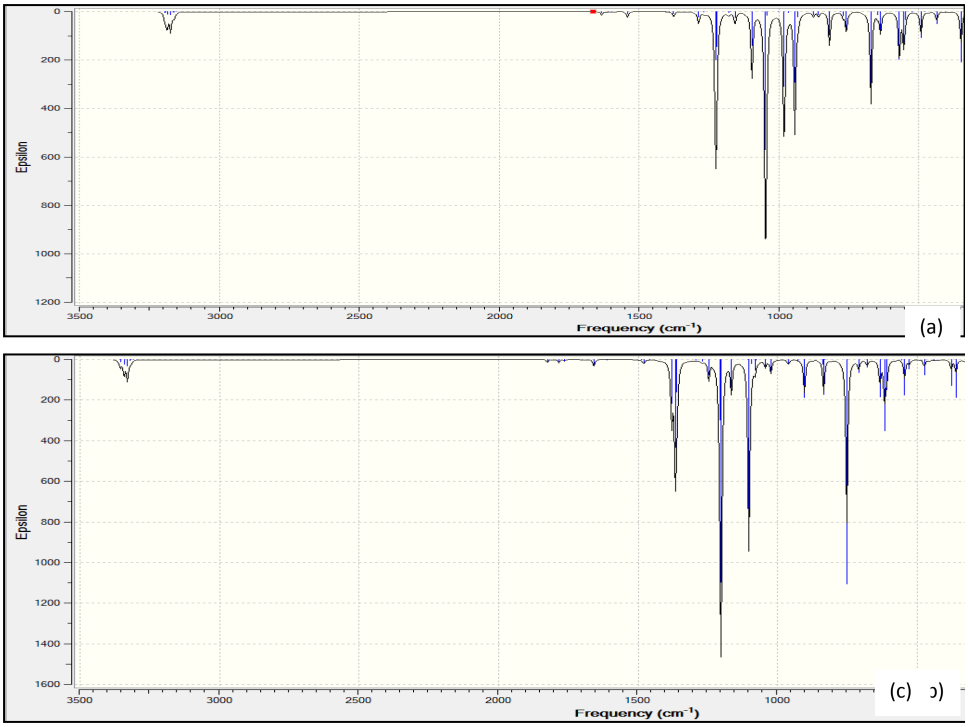
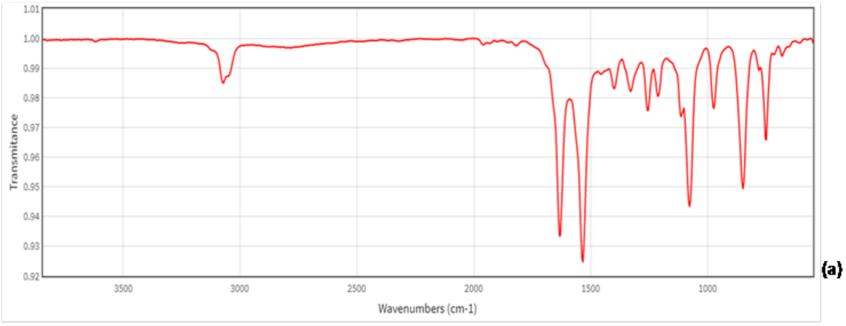


Figure 4 Experimental FT IR Spectrum (a) Normalized IR intensities of b) DFT method c) HF method for Naphthalene-2-sulfonic acid at B3LYP/ 6-311++G (d.2p) level



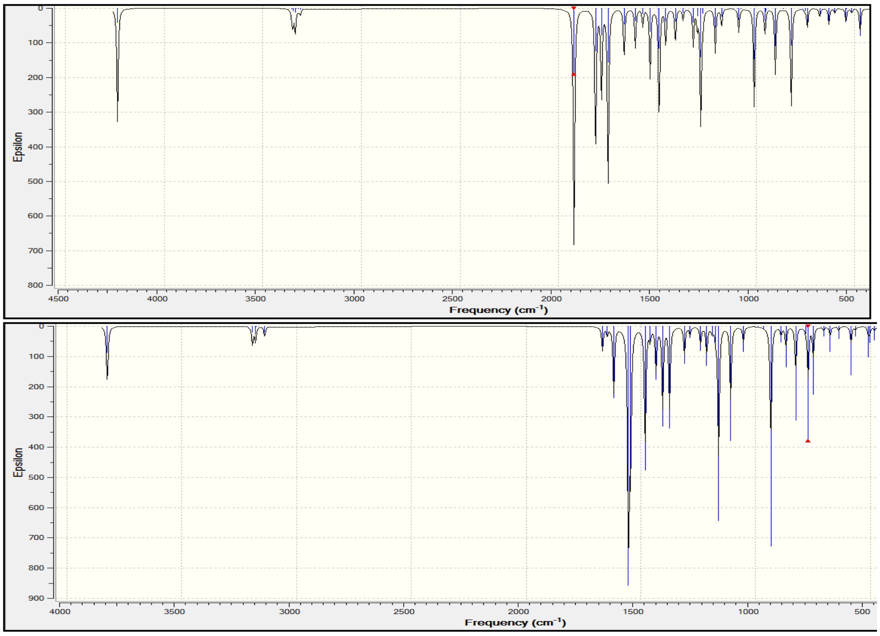


Figure 5 Experimental FT IR Spectrum (a) Normalized IR intensities of b) DFT method c) HF method for 1-Nitroso-2-naphthol at B3LYP/6-311++G (d.2p) level

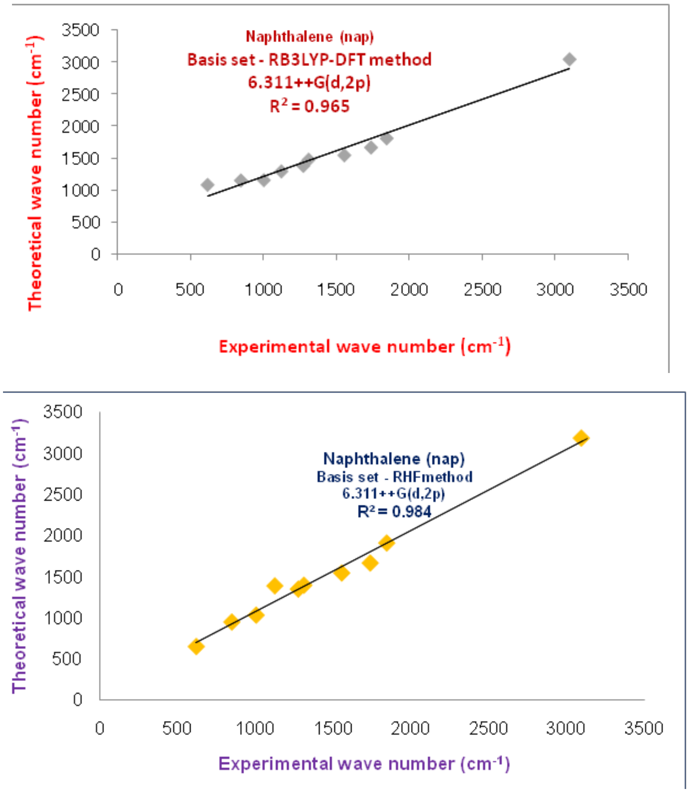


Figure 6 Graphic correlation between the experimental and theoretical frequencies of Naphthalene obtained by B3LYP /6.311++G(d,p) by DFT and HF methods

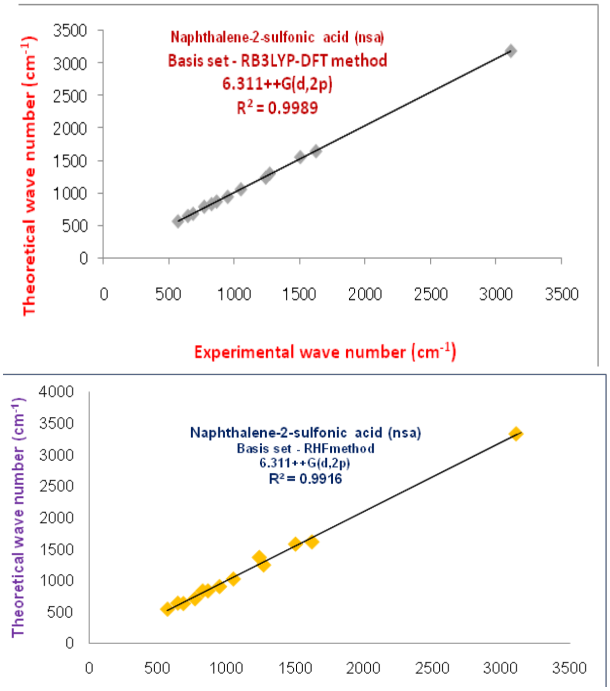


Figure 7 Graphic correlation between the experimental and theoretical Frequencies of Naphthalene-2-sulfonic acid obtained by B3LYP /6.311++G(d,p) by DFT and HF methods

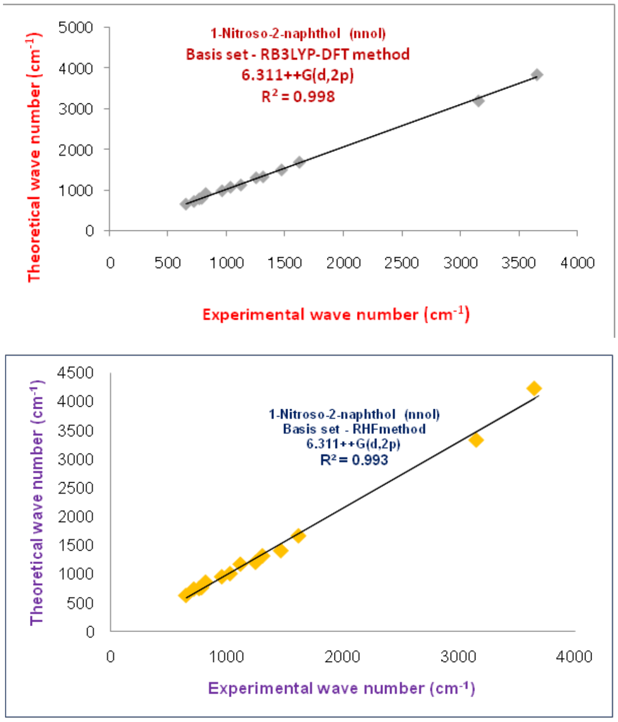


Figure 8 Graphic correlation between the experimental and theoretical Frequencies of 1-Nitroso-2-naphthol obtained by B3LYP /6.311++G(d,p) by DFT and HF methods

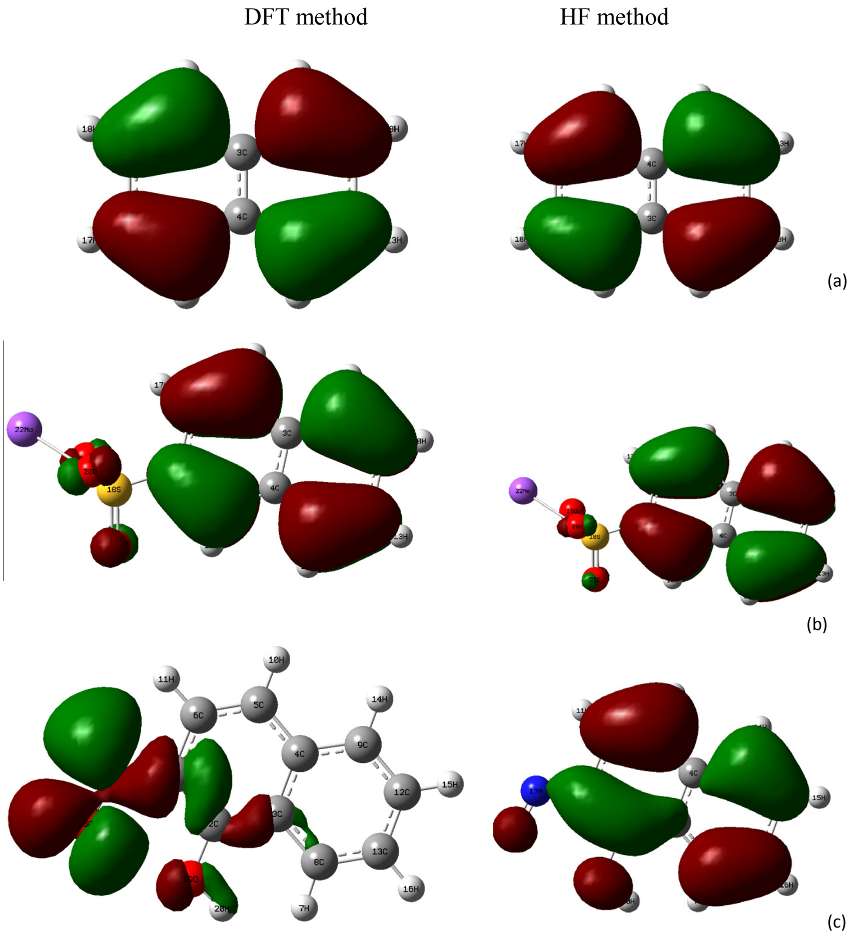
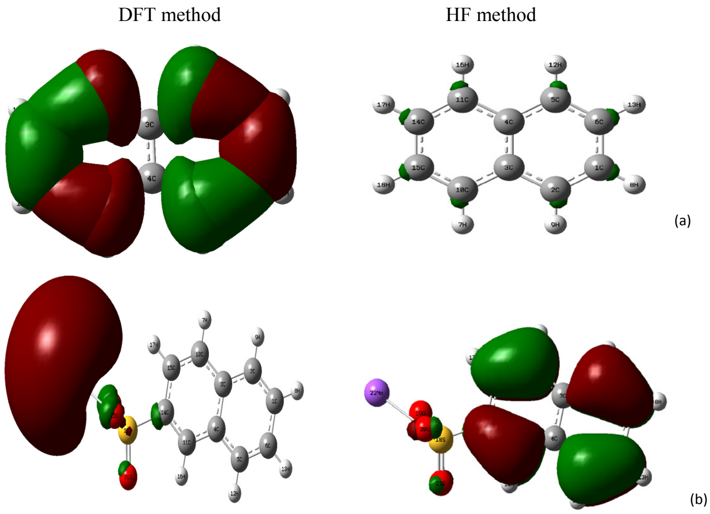


Figure 9 The HOMO orbitals of (a) Naphthalene (nap) (b) sodium salt of Naphthalene -2-sulfonic acid (nsa) and (c) 1-nitroso-2-naphthol (nnol) at B3LYP/6.311++ G(d,2p) level by DFT and HF methods



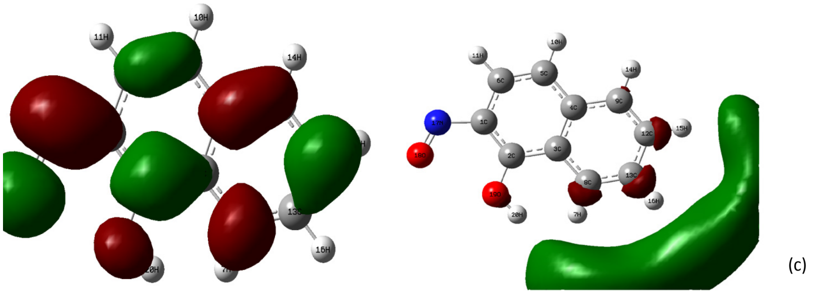


Figure 10 The LUMO orbitals of (a) Naphthalene (nap) (b) sodium salt of Naphthalene -2-sulfonic acid (nsa) and (c) 1-nitroso-2-naphthol (nnol) at B3LYP/6.311++ G(d,2p) level by DFT and HF methods

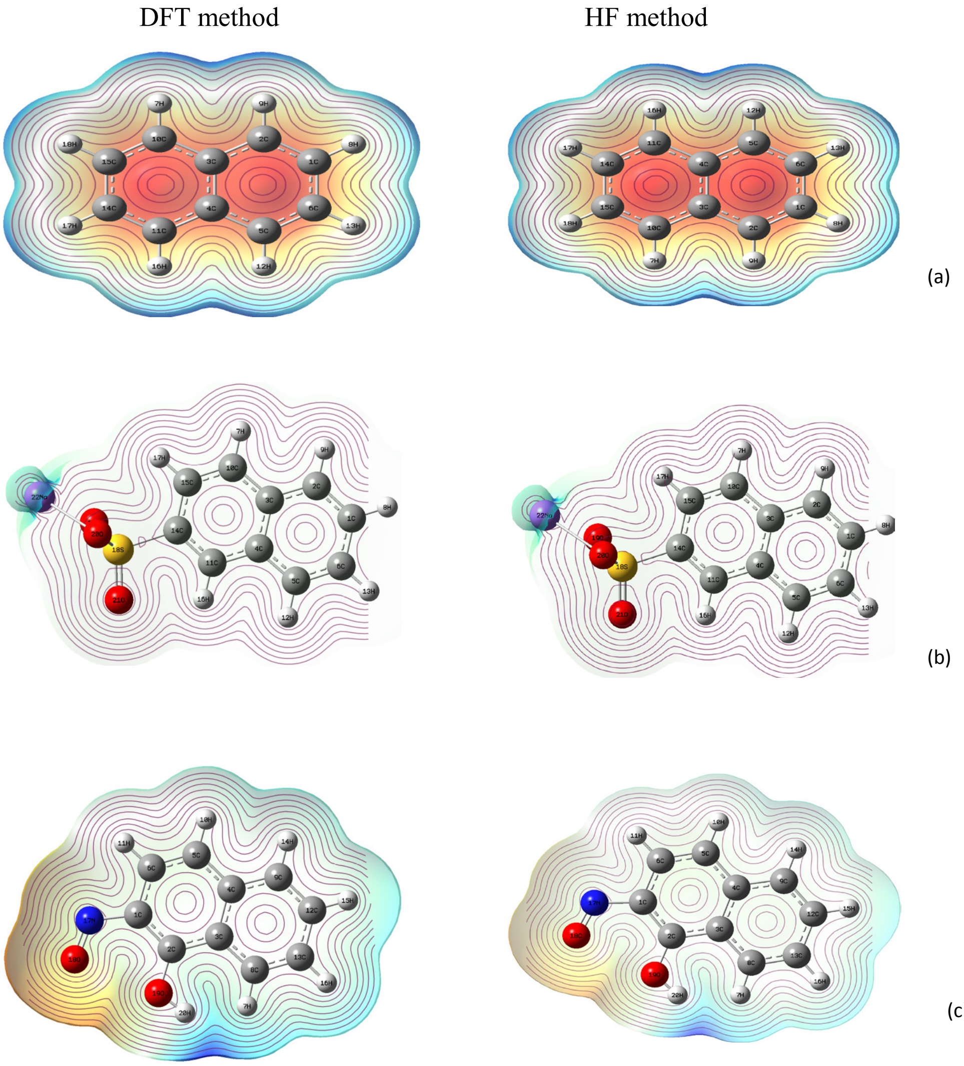


Figure 11 The Contour Map of molecular electrostatic potential surface of (a) Naphthalene (nap) (b) sodium salt of Naphthalene -2-sulfonic acid (nsa) and (c) 1-nitroso-2-naphthol (nnol) at B3LYP/6.311++ G(d,2p) level by DFT and HF methods

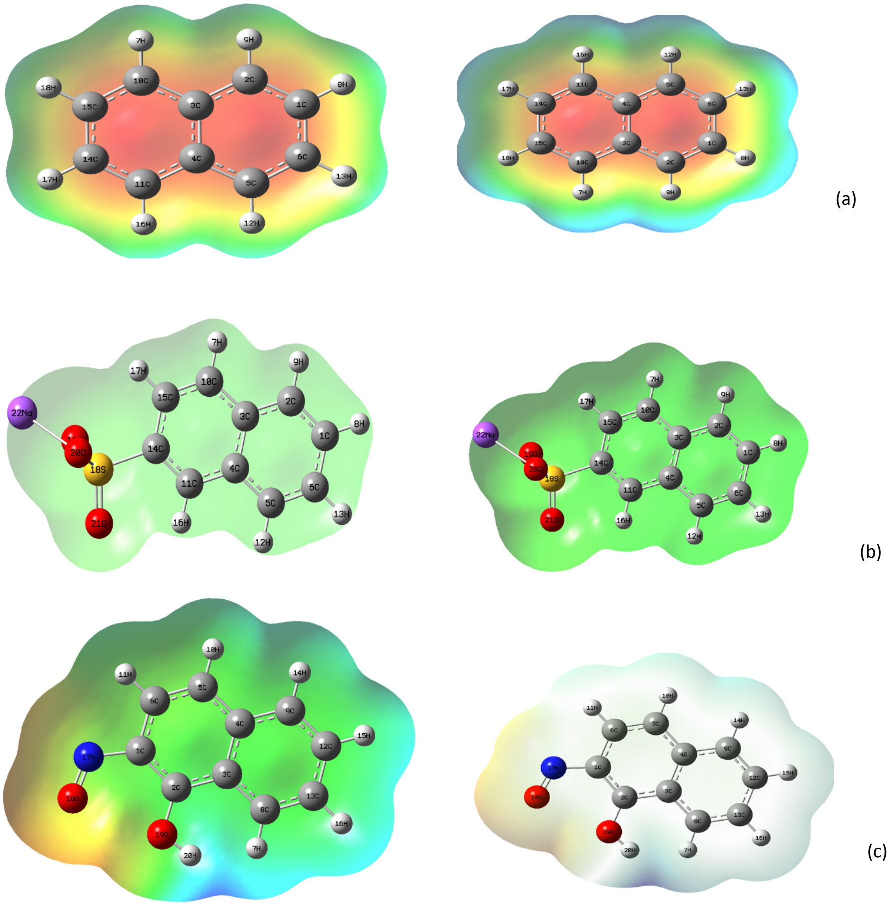


Figure 12 The Molecular electrostatic potential surface of Naphthalene (nap), (b) sodium salt of Naphthalene -2-sulfonic acid (nsa) and (c) 1-nitroso-2-naphthol (nnol) at B3LYP/6.311++ G(d,2p) level by DFT and HF methods