

## A Theoretical Study on Dopamine Molecule

 Lana O. Ahmed<sup>a</sup>,  Rebaz A. Omer<sup>b,c</sup>

<sup>a</sup> Department of physics, Faculty of Science & Health, Koya University, Koya KOY45, Kurdistan Region – F.R. Iraq.

<sup>b</sup> Department of Chemistry, Faculty of Science & Health, Koya University, Koya KOY45, Kurdistan Region – F.R. Iraq.

<sup>c</sup> Department of chemistry, Faculty of Science, Firat University, 23169 Elazig Turkey

### ABSTRACT

Now-days the computational quantum theory especially Hartree-Fock (HF) and Density functional theory (DFT) is an important role in physical chemistry. Dopamine is a hormone neurotransmitter that is why understanding the stability, reactivity and structure analysis are important. In this study, we optimize the geometrical structure of dopamine then we find the energy band gaps using different basis sets for both DFT and HF methods. We select 6-31G\* at DFT method for our dopamine molecule. IR and NMR spectra with some reference are investigated according to this method.

### ARTICLE INFO

*Keywords:*

Dopamine.

Bandgap energy.

DFT.

Hartree-Fock Theory

**Revised:** 02-December-2019

**Accepted:** 11-December-2019

**ISSN:** 2651-3080

### 1. Introduction

Dopamine is organic base like amine, the structure is consisting of benzene ring with amines and two hydroxyl groups, the molecular formula is  $C_8H_{11}NO_2$  and the nomenclature is 4-(2-aminoethyl)benzene-1,2-diol. Dopamine is hormone that plays important roles in human body and brain [1, 2]. Dopamine function in a brain is neurotransmitter, sends signals from released cell nerves to other cell nerves [3, 4]. The normal function of dopamine in a brain is ability storage in mind, learning, adjusting character and controlling noise level [5].

Several nervous system diseases caused by dysfunction of dopamine, such as Schizophrenia (SPh) and Parkinsones disease (PD) Schizophrenia (SPh) caused by dopamine activity levels and Parkinsones (PD) caused by decreasing dopamine secreted neuron in area of midbrain [6-9].

Attention deficit hyperactivity disorders (ADHD) involves decreasing dopamine activity [10]. Understanding the stability, reactivity and structure of dopamine is important for acting mechanisms in the human body and ability of binding to receptors [11]. Many researchers are focusing on the development of a sensitive method to measure dopamine which is important for certain diseases [12-14].

The resulting of nuclear magnetic resonance (NMR) and DFT was provided information of electrochemical properties of dopamine and understanding of dopamine activity neurotransmitter in aqueous solutions. DFT theoretical calculation with the basis set of 6-311++G (d,p) was analyzed various hydrogen bond of dopamine hydrochloride with H<sub>2</sub>O [15]. Different solvent as a medium was used for determining the oxidation of dopamine, especially water (H<sub>2</sub>O) [16].

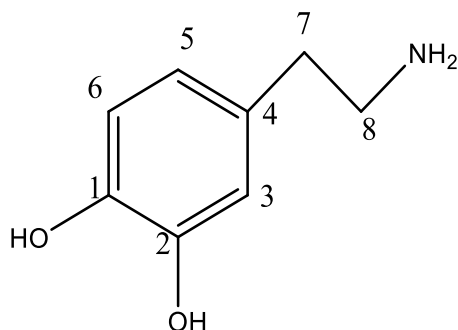
\* Corresponding author:

E-mail ([lane.omer@koyauniversity.org](mailto:lane.omer@koyauniversity.org))

In this study, we will explain and find the energy bandgaps by using Gaussian program software. The different basis sets (3-21G, 6-31G, 6-31G\*, 6-311G, LanL2DZ, LanL2MB and SDD) for two methods (DFT and HF) performed on dopamine geometry. We chose 6-31G\* at the DFT method to show the IR and NMR spectra for the geometry structure.

## 2. COMPUTATIONAL METHODS

The dopamine structure was drawn by Chem. Bio Draw Ultra 14.0 (Fig. 1). The structure of dopamine optimized by both density functional theory (DFT) and Hartree-Fock (HF) [9]. Different basis sets have been applied to find the energy bandgaps of dopamine for obtaining the real value of bandgap energy of dopamine. The reason why we use different basis sets is that each basis sets involves some special characteristics unlike another one [17]. Table 1 shows the energy band gaps for the two methods of different basis sets. The geometry system of dopamine at the B3LYP (DFT), 6-31G' basis set has been chosen [9, 18]. The frequency and NMR were calculated to this basis set [19]. The Gaussian 09 program has been used for all the calculations. Also, the origin program was performed for drawing the IR spectra as in Figure 3.



**Figure 1.** Structure of Dopamine

## 3. RESULT AND DISCUSSION

### 3.1. Energy bandgaps

The first task of the computational work is finding the optimized molecular structure using Gaussian 09 program. The energy bandgaps associated with basis sets (3-21G, 6-31G, 6-31G\*, 6-311G, LanL2DZ, LanL2MB and SDD) were listed in Table 1. As can be observed in the table the energy bandgaps for the Hartree-Fock (HF) method have higher values compared with the density functional theory (DFT). We selected the optimized structural parameter of dopamine with the 6-31G\* by the DFT method [9]. From Table 1, two values are very close to each other (6-31G and

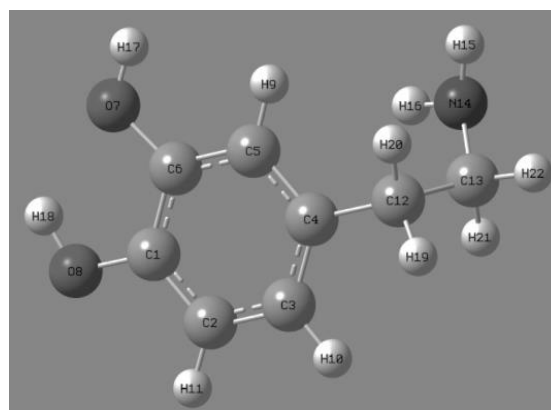
6-31G\*) but we chose 6-31G\* basis set for the reason it contains more parameters [19, 20].

**Table 1.** The energy bandgaps of different basis sets for both HF and DFT methods.

Basis sets	HF method Energy bandgaps (ev)	DFT method Energy bandgaps (ev)
3-21G	12.16685	5.56967
6-31G	12.08412	5.60531
6-31G*	12.08439	5.60558
6-311G	11.90970	5.56450
LanL2DZ	11.78071	5.45565
LanL2MB	13.51518	5.87607
SDD	11.78425	5.45592

### 3.2. Molecular Structure:

The molecular structure and numbering of atom in the dopamine molecule was shown in Figure 2. The 60 vibration modes are presenting in the molecule. The first task of computational work was optimized the molecule. The Gaussian programs viewed the number of atoms scheme. To calculate the geometric structure DFT was used.



**Figure 2:** Optimized molecular structure of Dopamine

### 3.3 Vibrational Assignments:

The vibrational frequency was calculated by the DFT method at 6-31G\* basis sets, FT-IR Figure 3 was observed with various vibration have been present in Table 2. The fundamental functional group was vibrated are discussed in the following.

#### 3.2.1. C-C /C=C vibrations:

The vibration carbone-carbone stretching in a ring usually occurs in a region 1400-1600  $\text{cm}^{-1}$  [21-23]. The

**Table 2.** Various vibration of atoms calculated by DFT (6-31G\*)

St. NO	vibration assignments	observed frequency (cm <sup>-1</sup> )	St. NO	vibration assignments	observed frequency (cm <sup>-1</sup> )
1	(C-H) out	43.77	32	(all H) ro	1181.68
2	(C-H) out	80.72	33	(all H) ro	1200.46
3	(C-H) out	128.26	34	(all H) ro	1227.25
4	(C-H) out	191.71	35	(all H) out,ro	1256.21
5	(C-H) out	249.98	36	(C1-O8)Sy,s	1281.71
6	(O7-H17)ro	273.63	37	(C4-C12)Sy,s	1326.77
7	(N14-H15,16)ro	283.72	38	(C12-C13)Sy,s	1358.67
8	(N14-H15,16)ro (C-O)ro	297.55	39	(C-C)in,Sy	1383.2
9	(C-H)out,ro	312.8	40	(all H)out, ro	1399.39
10	(C-H) out,ro	369.13	41	(C-C)in,Sy	1417.4
11	(C-H) out,ro	428.62	42	(C-C)in,Sy	1427.62
12	(C-H) out,ro	458.24	43	(C-C)in,Sy	1488.18
13	(C-H) out,ro	473.85	44	(C13-H21,22)sc	1527.34
14	(C-H) out,ro	490.4	45	(C12-H19,20)sc	1531.68
15	(C-H) out,ro	526.53	46	(C=C)in,Sy	1579.42
16	(N14-H15,16)ro	569.12	47	(C=C)in,Sy	1666.41
17	(C-C,C=C)in,ro	595.44	48	(C=C)in,Sy	1675.25
18	(C-C,C=C)in,ro	649.6	49	(N14-H15,16)sc	1709.1
19	(C-C,C=C)in,ro	723.66	50	(C12-H19,20)sy	3027.75
20	(C-C,C=C)in,ro	731.78	51	(C13-H21,22)sy	3043.08
21	(C-H) ro	794.48	52	(C12-H19,20)asy	3074.14
22	(C-H) ro	844.21	53	(C13-H21,22)asy	3094.4
23	(C-H) ro	857.95	54	(C5-H9)sy	3181.27
24	(C12-C13)sy	884.88	55	(C3-H10)sy	3199.5
25	(C12-C13)sy	896.45	56	(C2-H11)sy	3236.82
26	(C12-C13)sy	964.37	57	(N14-H15,16)sy	3551.73
27	(C-H)in,sc	976	58	(O8-H18)sy	3626.92
28	(C12-H19,20)ro	1020.82	59	(N14- H15,16)asy	3672.03
29	(C13-N14)sy	1103.82	60	(O7-H17)sy	3705.43
30	(O7-H17)ro	1126.49			
31	(C13-N14)sc	1152.66			

Abbreviation: out: out of the plane, ro: rocking, sy: symmetrical, asy: anti-symmetrical, in: in the plan, sc: Scissoring.

vibration of carbone-carbone of aromatic benzene ring was occurring in the region 1420-1625 cm<sup>-1</sup>. In aromatic ring such as benzene, has six-member rings, two or more vibrations occur due to the vibration of the skeletal, the strong vibration was started at 1500 cm<sup>-1</sup>. Moreover, the ring is conjugated by the atoms and also the vibration observed at 1580 cm<sup>-1</sup>. In the present work, the carbon-carbon starching vibration occurred in a region 1417.4-1675.25 cm<sup>-1</sup>. In the dopamine compound, the ethylamine was conjugated to the ring, the vibration peak was observed

at 1579 cm<sup>-1</sup>. The strong starching vibration of C=C in a ring occurred in a region 1579.42-1675.25 cm<sup>-1</sup>. It is symmetrical; this is caused by substituent of an aromatic ring. The vibration carbon-carbon single bond occurred at 1417.40-1488.18 cm<sup>-1</sup>. It is symmetrical vibration, but the stronger vibration for C-C in benzene ring was observed in the region 1488.18 cm<sup>-1</sup>. For ethylamine conjugated in the structure of dopamine the C-C (out of the plan) was vibrated in the region 1326.77-1385.67 cm<sup>-1</sup>. It vibrates symmetrical strongly. In 595.44, 649.6, 723.66 and 731.78 cm<sup>-1</sup> C-C and

C=C in the plan (in the ring) was rocking vibration but in the region 884.88, 896.45 and 964.37  $\text{cm}^{-1}$  was symmetrical Stretching.

### 3.2.2. C-H vibrations:

Commonly aromatic compounds were observed in the region 3000-3100  $\text{cm}^{-1}$  due to multiple weak bonds of C-H stretching vibration [24]. The C-H bending vibration in the plan was observed in the region 990-1390  $\text{cm}^{-1}$  and the peak was weak intensity [25]. The bond of C-H in the plane was very useful to find the characterization of the compounds [26]. When the carbon and hydrogen in the plane interacts each other, the vibration appears above 1200  $\text{cm}^{-1}$ , usually it moves in the opposite direction. [27, 28]. The C-H out of the plane usually occurs in the region 700-1000  $\text{cm}^{-1}$  [29, 30]. In our dopamine molecule the C-H vibrates symmetrical stretching out of the plane and it observed from 3027.75  $\text{cm}^{-1}$  to 3094.4  $\text{cm}^{-1}$ . Whereas the C-H in the plan was symmetrically vibrated between these two regions 3181.27-3236.82  $\text{cm}^{-1}$  this is an agreement with literature survey. In the region 3236.82- 526.53  $\text{cm}^{-1}$  all C-H out of the plan was rocking vibrations. Also, all hydrogen atoms were rocking vibrations in the dopamine molecule, these vibrations occurred in the region between 1181.68-1256.21  $\text{cm}^{-1}$ .

### 3.2.3. O-H vibrations:

In most of the literature survey show the O-H vibration for water was observed at the region 3700-3100  $\text{cm}^{-1}$ , but the phenolic compound occurred at 3600-3200  $\text{cm}^{-1}$  [31-33]. In our study, O-H symmetrical stretching was observed at 3626.92  $\text{cm}^{-1}$  for O8-H18, and for O7-H17 the symmetrical vibration was observed in the region 3705.43  $\text{cm}^{-1}$ . Both peaks are in a middle intensity due to the effect of substituent and the aromatic ring on the OH groups.

### 3.2.4. N-H vibrations:

The nitrogen and hydrogen stretching vibration peaks were observed in the region 3500-3350  $\text{cm}^{-1}$  and 1650 to 1550  $\text{cm}^{-1}$  [34]. In our dopamine N-H bond, symmetrically vibrated at 3551.73  $\text{cm}^{-1}$ . Meanwhile at 569.12, 283.72 and 297.55  $\text{cm}^{-1}$  was rocking. Also scissoring occurred in the region 1709.1  $\text{cm}^{-1}$ .

### 3.2.5. C-N vibration

In this study of dopamine structure was shown the vibration of C-N in the region 1103.82  $\text{cm}^{-1}$  was symmetrical and in a region, 1152.66  $\text{cm}^{-1}$  was scissoring.

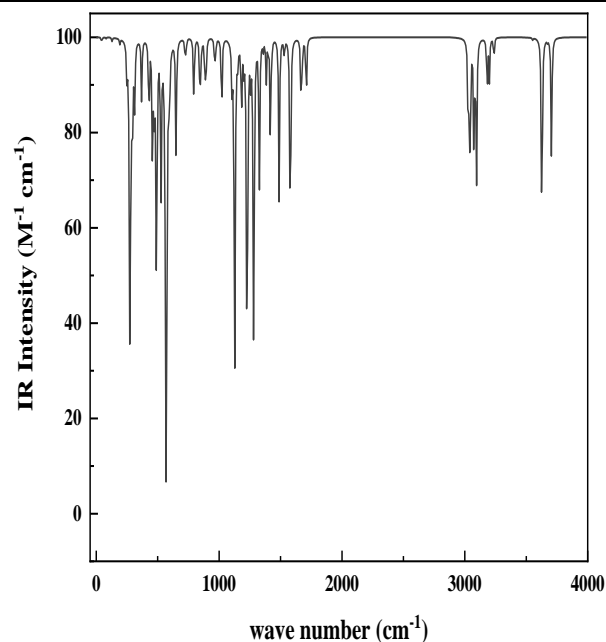


Figure 3. FT-IR Spectrum of Dopamine.

### 3.3. NMR analysis

The  $^{13}\text{C}$  NMR chemical shifts used to identify chemical compounds [35]. GIAO (Gauge Including Atomic Orbital) is the fastest procedure for calculation upon the basis set used. A GIAO method was preferable for many aspects state of the subject [36]. NMR used for calculating chemical shifts of the title compound on the basic TMS HF/6-31G(d)GIAO, TMS B3LYP/6-311+G(2d,P)GIAO, and CH4 HF/6-31G(d)GIAO for carbon atoms. Hydrogen and nitrogen on the basic TMS HF/6-31G(d)GIAO, TMS B3LYP/6-311+G(2d, P)GIAO and oxygen on the basic H<sub>2</sub>O B3LYP/6-311+G(2d,P)GIAO, H<sub>2</sub>O HF/6-31G(d)GIAO. Table 3 showed the  $^{13}\text{C}$

NMR for all references. According to TMS HF/6-31G(d) reference, the carbon was ordered from C3>C1>C4>C6> C5>C2> C12>C13 that means carbon number C3 had highest ppm and lowest filed but C13 had lowest ppm and highest filed. However, for TMS b3LYP/6-311+G(2d, P) reference for carbon atoms was ordered from C6>C1>C3>C4 >C2>C5>C13>C12, in this reference C6 observed at highest ppm lowest filed but C12 had lowest ppm and highest filed. For the reference CH4 HF/6-31 G(d), C1>C6>C4>C3>C2>C5>C13>C12 carbon number one (C1) represented in highest ppm and carbon number twelve found in lowest ppm and higher filed. For H-NMR Table 4 there were two references: TMS HF/6-31 G(d)GIAO and TMS B3LYP/6-311+G(2d,P)GIAO. According to the reference TMS HF/6-31G(d)GIAO the observation hydrogen peak started from highest filed (H15) to the end of lowest filed (H11). H11>H10>H9>H18>H22>H17>H21>H19>H20>H16>H15. Besides for reference TMS B3LYP/6-

311+G(2d,P) GIAO the order of hydrogen peak is the same as the previous reference with a little bit difference in a lower ppm for all hydrogen atoms. The NMR for nitrogen shown in Table 5, the peak was observed at 19.98 ppm for TMS HF/6-31G(d)GIAO, but for TMS B3LYP/6-311+G(2d,P)GIAO was observed at 17.5ppm. The peak for two oxygen (O7 and O8) in a dopamine molecule occurred at 88.9ppm and 94.5ppm respectively according to H2O HF/6-31 G(d)GIAO, but for H2O B3LYP/6-311+G(2d, P)GIAO reference both oxygen (O7 and O8) peaks decreased for lower ppm 85.8 and 91.5 respectively, as it shown in the Table 6.

**Table 3.** The observed C NMR chemical shifts in ppm for Dopamine

C. NO	NONE ppm	TMS HF/6-31 G(d) GIAO ppm	TMS B3LYP/6-311+G(2d,P) GIAO ppm	CH4 HF/6-31 G(d) GIAO ppm
C1	54	146	151.9	145
C2	80.9	120.7	102	118.3
C3	75	155	132.7	124.1
C4	55.7	145.8	123	133.9
C5	84	124	98.3	115
C6	56	144	153.9	143.1
C12	151	71	31.9	48.1
C13	149	69	33.8	50.1

**Table 4.** The observed H NMR chemical shifts in ppm for Dopamine

H. NO	NONE ppm	TMS HF/6-31 G(d) GIAO ppm	TMS B3LYP/6-311+G(2d,P) GIAO ppm
H9	26.79	5.81	5.1
H10	26.1	6.5	5.78
H11	25.83	6.7	6.0
H15	33.2	- 0.6	- 1.31
H16	32.41	0.9	- 0.58
H17	29.85	2.75	2.05
H18	27.6	5.0	4.28
H19	30.25	2.31	1.61
H20	30.8	1.8	1.1
H21	30.05	2.55	1.58
H22	29.78	2.82	2.13

**Table 5.** The observed Nitrogen atom NMR chemical shifts in ppm for Dopamine

N. NO	NONE ppm	TMS HF/6-31 G(d) GIAO ppm	TMS B3LYP/6-311+G(2d,P) GIAO ppm
N14	240.9	19.98	17.5

**Table 6.** The observed Oxygen atom NMR chemical shifts in ppm for Dopamine

O. NO	NONE ppm	H <sub>2</sub> O HF/6-31 G(d) GIAO	H <sub>2</sub> O B3LYP/6-311+G(2d,P) GIAO
O7	234.25	88.9	85.8
O8	228.6	94.5	91.5

#### 4. CONCLUSION

In this work, all basis sets with both HF and DFT methods investigated to calculate bandgap energies for dopamine molecule. The energy bandgaps for HF approximation are larger than the energy bandgaps for DFT method. Proposed the better basis set is 6-31G\* according to the previous literature, this basis set for DFT method is very close to the real value of dopamine. The IR shows the vibration for all atoms that is good agreement with the kinds of literature. NMR has been used to identify the molecular structure. The peaks of atoms in NMR related to the types of the references. For example, C1 has different shifted in a ppm for all three references. For nitrogen and hydrogen there were only TMS HF/6-31 G(d)GIAO and TMS B3LYP/6-311+G(2d, P). The chemical shifts were different for different references. The reference H2O HF/6-31 G(d)GIAO and H2O B3LYP/6-311+G(2d, P)GIAO show the oxygen's ppm and it is closed to each other.

#### AKNOLOGMENT

We would like to thank Firat University, physics department especially the head of the physics department for supporting this study.

#### REFERENCES

- Gulledge, A.T. and D.B. Jaffe, *Dopamine decreases the excitability of layer V pyramidal cells in the rat prefrontal cortex*. Journal of Neuroscience, 1998. **18**(21): p. 9139-9151.
- Tzschentke, T., *Pharmacology and behavioral pharmacology of the mesocortical dopamine system*. Progress in neurobiology, 2001. **63**(3): p. 241-320.
- Goldman-Rakic, P.S., E.C. Muly III, and G.V. Williams, *D<sub>1</sub> receptors in prefrontal cells and circuits*. Brain Research Reviews, 2000.
- Nicola, S.M., D.J. Surmeier, and R.C. Malenka, *Dopaminergic modulation of neuronal excitability in the striatum and nucleus accumbens*. Annual review of neuroscience, 2000. **23**(1): p. 185-215.
- Santos-García, D., M. Prieto-Formoso, and R. de la Fuente-Fernández, *Levodopa dosage determines adherence to long-acting dopamine agonists in*

- Parkinson's disease*. Journal of the neurological sciences, 2012. **318**(1-2): p. 90-93.
6. Barforushi, M.M., S. Safari, and M. Monajjemi, *Nano Biotechnology Study of X-Dopamine Complexes (X= Co<sup>2+</sup>, Au<sup>3+</sup>, Pt<sup>2+</sup>, and Pd<sup>2+</sup>)*. Journal of Computational and Theoretical Nanoscience, 2015. **12**(10): p. 3058-3065.
  7. Aliste, M.P., *Theoretical study of dopamine. Application of the HSAB principle to the study of drug-receptor interactions*. Journal of Molecular Structure: THEOCHEM, 2000. **507**(1-3): p. 1-10.
  8. Fellous, J.-M. and R. Suri, *Dopamine, roles of*. The handbook of brain theory and neural networks, 2003: p. 361-365.
  9. Mehdizadeh Barforushi, M. and K. Zare, *A Theoretical Study on Dopamine: Geometry, energies and NMR*. Journal of Physical & Theoretical Chemistry, 2014. **11**(2): p. 57-61.
  10. Gingrich, J.A. and M.G. Caron, *Recent advances in the molecular biology of dopamine receptors*. Annual review of neuroscience, 1993. **16**(1): p. 299-321.
  11. Barforushi, M.M., *NMR and NBO investigation of Dopamine properties in point view of Brain activities*. Oriental Journal of Chemistry, 2014. **30**(4): p. 1823-1840.
  12. Raghu, P., et al., *A novel horseradish peroxidase biosensor towards the detection of dopamine: A voltammetric study*. Enzyme and microbial technology, 2014. **57**: p. 8-15.
  13. Sun, W., et al., *Poly (methylene blue) functionalized graphene modified carbon ionic liquid electrode for the electrochemical detection of dopamine*. Analytica chimica acta, 2012. **751**: p. 59-65.
  14. Yu, D., et al., *A novel electrochemical sensor for determination of dopamine based on AuNPs@ SiO<sub>2</sub> core-shell imprinted composite*. Biosensors and Bioelectronics, 2012. **38**(1): p. 270-277.
  15. Zhai, C., et al., *Experimental and theoretical study on the interaction of dopamine hydrochloride with H<sub>2</sub>O*. Journal of Molecular Liquids, 2016. **215**: p. 481-485.
  16. Chen, S., K.Y. Tai, and R.D. Webster, *The Effect of the Buffering Capacity of the Supporting Electrolyte on the Electrochemical Oxidation of Dopamine and 4-Methylcatechol in Aqueous and Nonaqueous Solvents*. Chemistry—An Asian Journal, 2011. **6**(6): p. 1492-1499.
  17. Mamand, D., *Determination the band gap energy of poly benzimidazobenzophenanthroline and comparison between HF and DFT for three different basis sets*. Journal of Physical Chemistry and Functional Materials. **2**(1): p. 31-35.
  18. Frisch, M.J., J.A. Pople, and J.S. Binkley, *Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets*. The Journal of chemical physics, 1984. **80**(7): p. 3265-3269.
  19. Gh, A.B., *Ab initio study, investigation of NMR shielding tensors, NBO and vibrational frequency of catechol thioethers*. Bulletin of the Chemical Society of Ethiopia, 2010. **24**(2).
  20. Nagy, P.I., G. Alagona, and C. Ghio, *Theoretical studies on the conformation of protonated dopamine in the gas phase and in aqueous solution*. Journal of the American Chemical Society, 1999. **121**(20): p. 4804-4815.
  21. Socrates, G., *Infrared and Raman characteristic group frequencies: tables and charts*. 2004: John Wiley & Sons.
  22. Tammer, M., *G. Sokrates: Infrared and Raman characteristic group frequencies: tables and charts*. 2004, Springer.
  23. Jeyavijayan, S. and M. Arivazhagan, *Study of density functional theory and vibrational spectra of hypoxanthine*. 2010.
  24. Krishnakumar, V. and R.J. Xavier, *Normal coordinate analysis of 2-mercapto and 4, 6-dihydroxy-2-mercapto pyrimidines*. 2003.
  25. Srivastava, A. and V. Singh, *Theoretical and experimental studies of vibrational spectra of naphthalene and its cation*. 2007.
  26. Wilson, E.B., J.C. Decius, and P.C. Cross, *Molecular vibrations: the theory of infrared and Raman vibrational spectra*. 1980: Courier Corporation.
  27. Ramalingam, S., et al., *FTIR and FTRaman spectra, assignments, ab initio HF and DFT analysis of 4-nitrotoluene*. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2010. **75**(4): p. 1308-1314.
  28. Nagabalasubramanian, P., et al., *FTIR and FT Raman spectra, vibrational assignments, ab initio, DFT and normal coordinate analysis of  $\alpha$ ,  $\alpha$  dichlorotoluene*. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2009. **73**(2): p. 277-280.
  29. Nagabalasubramanian, P., S. Periandy, and S. Mohan, *Ab initio HF and DFT simulations, FT-IR and FT-Raman vibrational analysis of  $\alpha$ -chlorotoluene*. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2010. **77**(1): p. 150-159.
  30. Krishnakumar, V., V. Balachandran, and T. Chithambarathanu, *Density functional theory study of the FT-IR spectra of phthalimide and N-bromophthalimide*. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2005. **62**(4-5): p. 918-925.
  31. Besson, G. and V. Drits, *Refined relationships between chemical composition of dioctahedral fine-grained micaceous minerals and their infrared spectra within the OH stretching region. Part II: The main factors affecting OH vibrations and quantitative analysis*. Clays and Clay Minerals, 1997. **45**(2): p. 170-183.
  32. Zviagina, B.B., et al., *Interpretation of infrared spectra of dioctahedral smectites in the region of OH-stretching vibrations*. Clays and Clay Minerals, 2004. **52**(4): p. 399-410.

33. Sun, Q., *The Raman OH stretching bands of liquid water*. *Vibrational Spectroscopy*, 2009. **51**(2): p. 213-217.
34. Serra-Crespo, P., et al., *Interplay of metal node and amine functionality in NH<sub>2</sub>-MIL-53: modulating breathing behavior through intra-framework interactions*. *Langmuir*, 2012. **28**(35): p. 12916-12922.
35. Subramanian, N., N. Sundaraganesan, and J. Jayabharathi, *Molecular structure, spectroscopic (FT-IR, FT-Raman, NMR, UV) studies and first-order molecular hyperpolarizabilities of 1, 2-bis (3-methoxy-4-hydroxybenzylidene) hydrazine by density functional method*. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2010. **76**(2): p. 259-269.
36. Ditchfield, R., *Molecular orbital theory of magnetic shielding and magnetic susceptibility*. *The Journal of Chemical Physics*, 1972. **56**(11): p. 5688-5691.