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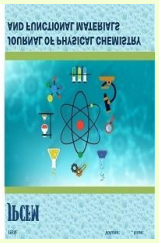

Serotonin: Structural Characterization and Determination of the Band Gap Energy

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ABSTRACT

Density function theory and Hartree-Fock approximation were used to optimize serotonin molecules with different basis set to find out its bandgap. By comparison with literature, we chose DFT with a basis set SDD. The vibrational spectra analysis of serotonin was analyzed and FTIR and NMR spectra analysis of the titled molecule was viewed for the preferred basis set.

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1. Introduction

Serotonin or monoamine neurotransmitter is a necessary biogenic amino alkane, that is biochemically derived from tryptophan [1] in a two-step mechanism, that's later consumed by the reaction of the amino and created monoamine [2], Figure1. Shows monoamine neurotransmitter chemical structure.

Monoamine is associated with add endogenous chemical messenger and can be found among the human brain between nerves. It's accountable for exploit moods and happiness [3]. This organic compound is manufactured in the brain and thus the intestines and thus the bulk of the Serotonin is found among the gastrointestinal tract where it's accustomed to regulate organ movements [4]. The Serotonin level controls the varied activity processes [5,6]. Monoamine neurotransmitter, in addition, plays an awfully vital role to manage temperature, pressure, and sleek muscle functions. The recent study shows that monoamine plays a key role in disorder and respiratory disease [7]. Drugs, which could alter the monoamine level, is utilized within the treatment of depression. Recently, monoamine and its receptors become a difficulty of considerable interest. For drug manipulation, it is necessary to know the most points of the physical and chemical properties of an energetic compound. As a biologically very important molecule, the study of this compound is very important from the structural and analysis purpose of browse. Lots of researchers have done their research in different field supported this biomolecule [8-17]. The conformational analysis of monoamine in particle was investigated by modification of the alkane series by J. Pratuangdejkul and et al. [18]. They disbursed the method calculations altogether the four species by B3LYP/ 6-31 G(d,p) level of theory. They found that the simple physics cycle of proton-dissociation reaction is accustomed to living the pka1 value. There is an honest agreement between the experimental and theoretical calculations had observed. L. F. Pisterzi and et al. [19] determined the conformations of the aromatic radical and thus the protonated ethylamine aspect chain of monoamine by B3LYP/6-31G(d) levels of theory among the gas section.

In the present work, we show theoretically spectroscopic investigation of serotonin by using the DFT

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method with a basis set SDD to insight its property with IR and NMR spectroscopy.

2. Theoretical methodology

The optimization of serotonin structure has been performed by Density Function theory (DFT) and Hartree-Fock theory. We have applied different basis sets to find bandgap energy of serotonin because each of them has certain characteristics [36]. The bandgap in the monomer state of serotonin has been found to be (-7.165 eV) [37]. We have chosen DFT with a basis set SDD in table 1 because this set is more accurate than others and the value of bandgap is close to the value in the literature. Vibrational analysis of serotonin monomer state is performed and NMR is calculated for the chosen basis set by using Gauss Software.

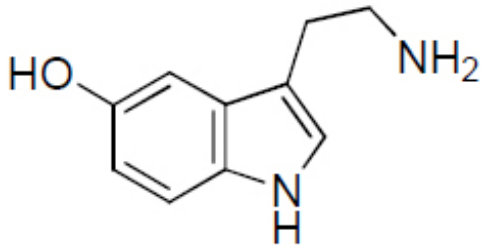

Figure 1. Chemical Structure of Serotonin

3. Result and Discussion

3.1. Molecular Structure

We have optimized the serotonin molecule computationally using Gaussian software with HF and DFT theory. Our interested biomolecule has 25 atoms and 69 normal modes present in it. Figure (1. b) shows the atomic numbers of serotonin which is drowned by Gauss software. Then the geometric structure is calculated with DFT and SDD basis set.

Table 1. Bandgap energy of Serotonin for different basis sets with HF and DFT methods.

Basis sets	HF method Energy gaps (ev)	DFT method Energy gaps (ev)
3-21G	11.2847	5.1011
6-31G	11.1554	5.0823
6-31G*	11.0253	5.0823
6-311G	10.8397	5.0361
LanL2DZ	12.5889	4.9419
LanL2MB	12.5845	5.3789
SDD	10.8438	4.9405

3.2. Energy bandgap

In order to determine the exact value of the bandgap energy of serotonin, it is necessary to exam different basis sets, because each of them has special characteristics that differ from another. Table 1. Illustrate the value of bandgap. We have realized from the table's data that each of the results has some defects and the HF approximation is not fit to run the serotonin structure. Because there is a large difference between the bandgap values which is impossible. The absolute error for each of basis sets from (3-21 G) up to (SDD) is (4.1, 4.0, 3.9, 3.7, 5.4, 5.4, 3.7) respectively. But the absolute error of bandgap energy for DFT for the same basis sets is (2.1, 2.0, 2.0, 2.2, 2.2, 1.7, 2.2) respectively. Accordingly DFT with basis set SDD can accept the result, in fact, it is not exactly real value but is better than HF approximation. [36] So that the structural analysis of serotonin state is performed by DFT with an SDD basis set in our study.

3.3 Vibrational assignments

The vibrational spectra analysis of the monomer state of serotonin has been performed by using DFT with an SDD basis set. Figure 3 shows the theoretical frequencies of the serotonin monomer. The vibrated functional group is discussed in the following:

3.2.1. 3.3.1 $C-H$ Vibrations

The $C-H$ stretching characteristics is observed in between 3000 and 3100 cm^{-1} for the aromatic benzene ring [23-26]. In Serotonin monomer, the $C-H$ stretching is calculated at 3240.53 cm^{-1}, 3202.14 $cm^{-1}$and 3182.61 cm^{-1}. The $C-H$ stretching in the alkyl side chain of Serotonin are observed in 2840-3010 cm^{-1} [20_bookmark33]. The aliphatic $C-H$ stretching vibration is calculated at 2964 cm^{-1}. In monomer, the asymmetric stretching vibrations are calculated at 3202.14 cm^{-1}. The CH_2 bending vibrations in the Serotonin monomer is calculated at 1422.62 cm^{-1}. In Serotonin monomer the $C-H$ in plane bending vibration is calculated at 1267.24 cm^{-1}.

3.2.2. Amino group vibrations

The $N-H$ stretching is generally observed in between 3300 and 3500 cm^{-1} [27]. In Serotonin the $N-H$ stretching was reported at 3696.92 cm^{-1} [20]. The position of the vibration in this region depends on the degree of hydrogen bonding and upon the physical state of the sample. The NH_2 asymmetric stretching in the Serotonin monomer is calculated at 3664.05 cm^{-1}. The NH_2 bending vibration in the Serotonin monomer appears at 3539.50 cm^{-1}[24].

3.2.3. COH group vibrations

The $C-O$ stretching vibration in Serotonin monomer is calculated at 1234.89 cm^{-1}, 1256.92 cm^{-1} and 1267.24 cm^{-1} respectively. It shows a good agreement with the data of Serotonin found in the literature [21].

The $O-H$ group generally gives three types of vibrations, i.e. stretching, in-plane bending and out of plane bending vibrations. The $O-H$ stretching vibrations generally occur in the region of 3500 cm^{-1} [28]. As reported earlier, the $O-H$ stretching vibration in Serotonin is found at 3607 ± 1 [20]. Tracy A. LeGreve and et al. had reported the $O-H$ stretching vibration in between 3672 and 3667 cm^{-1} [22]. In our title molecule, the $O-H$ stretching vibration in the monomer state appears at 3710.12 cm^{-1}. The $O-H$ in-plane bending vibration is calculated at 1234.89 cm^{-1}.

3.2.4. Serotonin ring vibrations

The aromatic ring $C=C$ stretching vibrations are arises in between 1600 and 1350 cm^{-1} [29-33]. In Serotonin monomer the $C=C$ ring vibrations are assigned at 1674.76 cm^{-1}, 1641.00 cm^{-1}, 1600.83 cm^{-1}, 1516.44 cm^{-1} and 1513.82 cm^{-1} respectively. The $C=C$ ring stretching vibrations shows an excellent agreement with the previously reported data of Serotonin [21].

The $C-C$ in-plane bending ring vibrations occur in the region below 1000 cm^{-1}[34, 35]. In our present work the $C-C-C$ in-plane bending vibrations are calculated at 945.06 cm^{-1}, 839.53 cm^{-1}, 832.52 cm^{-1}, 785.89 cm^{-1}, 768.53 cm^{-1},725.70 cm^{-1}, 665.32 cm^{-1}, 615.65 cm^{-1}.The out of plane bending vibration occurs at a lower wavenumber side in addition to in-plane bending vibration.

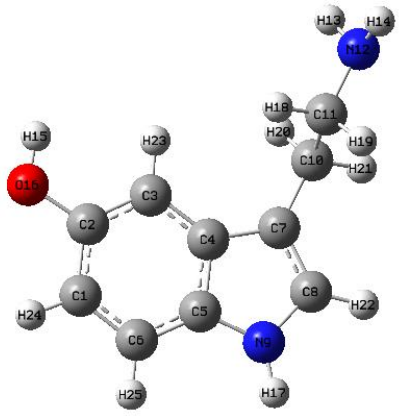

Figure 2. Serotonin structure $C_{10}H_{12}N_2O$.

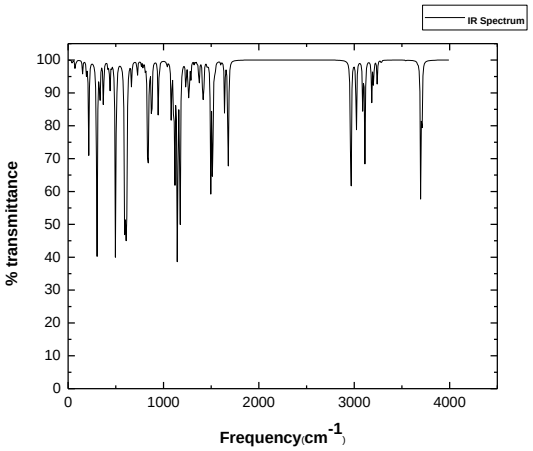

Figure 3. FT-IR Spectrum of Serotonin

4. NMR Analysis

NMR spectroscopy is a great tool for determining the structures of organic compounds. In order to identify chemical compounds in various samples, the 13-C NMR chemical shifts are used. We have used NMR to calculate chemical shifts for the serotonin compound. Figure 2 shows the Serotonin structure which is drawn by Gauss software. Moreover ; Table 2 shows the 13C NMR for all references, from the data in the table the carbons can be ordered as (C2>C5>C4>C8>C7>C1>C6>C3>C11>C10) for all references which means carbon number C3 was higher ppm

Table 2. The observed C NMR chemical shifts in ppm for Serotonin

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	76.6	123.4	105.9	122.5
C2	36.7	163.2	145.7	162.5
C3	86.03	113.8	96.5	113.3
C4	62	137.8	120.4	136.9
C5	57.2	142.6	125.2	141.9
C6	77.51	122.5	104.84	121.5
C7	73.6	126.2	108.9	125.6
C8	65.5	134.4	116.9	133.5
C10	156.4	43.5	26	42.6
C11	144.01	55.9	38.4	55.1

Table 3. The observed H NMR chemical shifts in ppm for Serotonin.

H. NO	NONE Ppm	TMS HF/6-31 G(d) ppm	TMS B3LYP/6-311+G(2d, P) ppm
H13	32.5	0.04	-0.67
H14	32.1	0.5	-0.17
H15	28.9	3.6	2.9
H17	26.1	6.6	5.8
H18	29.3	3.3	2.6
H19	30.1	2.5	1.8
H20	30.3	2.3	1.6
H21	29.7	2.9	2.1
H22	25.8	6.8	6.1
H23	26.2	6.5	5.7
H24	25.3	7.3	6.6
H25	25.6	7.0	6.3

Table 4. The observed Nitrogen atom NMR chemical shifts in ppm for Serotonin.

N. NO	NONE ppm	NH3 HF/6-31 G(d)GIAO ppm	NH3 B3LYP/6-311+G(2d,P)GIAO ppm
N9	124.1	136.6	134.4
N12	228.0	32.7	30.3

Table 5. The observed Oxygen atom NMR chemical shifts in ppm for Serotonin.

O. NO	NONE ppm	H2O HF/6-31 G(d) GIAO ppm	H2O B3LYP/6-311+G(2d, P)GIAO ppm
O16	198.9	124.3	121.1

lower filed but C13 was lower ppm higher filed. In addition, table 3 shows H- NMR for different references. According to the table for all references the hydrogen peak started from the higher field (H13) to lower field as (H24>H25>H22>H17>H23>H15>H18>H21>H19>H20> H14>H13). The peak for two Nitrogen N9, N12 in serotonin is viewed at 136.6 ppm and 32.7 ppm respectively for reference H2O HF/6-31 G(d)GIAO, but for H2O B3LYP/6-311+G(2d, P) GIAO reference both N9, N12 peaks has decreased for lower ppm 134.4 and 30.3 respectively which is shown in Table 4. Oxygen NMR is shown in Table5 and its peak has occurred at 124.3 ppm for TMS HF/6-31 G(d)GIAO, but for TMS B3LYP/6-311+G(2d, P) GIAO was observed at 121.1ppm.

5. CONCLUSION

The geometrical optimization of serotonin was investigated and analyzed by using different basis sets. The bandgap energy of the molecule was found. Vibrational normal modes of serotonin monomer were discussed and reported. NMR signal peaks were explained to determine the chemical structure of the molecule.

REFERENCES

[1] D.G. Flores, B. Velardo, M. Garrido, D.G. Gomez, M. Lozano, M.C. Ayuso,C. Barriga, S.D. Paredes, A.B. Rodríguez, J. Food Nutr. Res. 50 (2011) 229-236.

[2] J.V.V. Weele, G.M. Anderson, E.H. Cook, Eur. J. Pharmacol. 410 (2000) 165-181.

[3] S.N. Youn, Rev. Psychiatr. Neurosci. 32 (2007) 394-399.

[4] M. Berger, J.A. Gray, B.L. Roth, Annu. Rev. Med. 60 (2009) 355-366.

[5] D. Hoyer, J.P. Hannon, G.R. Martin, Pharmacol. Biochem. Behav. 71 (2002) 533e554.

[6] E.H. Decloedt, D.J. Stein, Neuropsychiatr. Disorder Treat. 6 (2010) 233-242.

[7] T.J. Pucadyil, S. Kalipatnapu, A. Chattopadhyay, Cell. Mol. Neurobiol. 25 (2005) 553-580.

[8] J. Almac, J. Molina, D. Menegaz, A.N. Pronin, A. Tamayo, V. Slepak, P. Berggren, A. Caicedo, Cell Rep. 17 (2016) 3281-3291.

[9] Y. Gao, T. Yao, Z. Deng, J. Sohn, J. Sun, Y. Huang, X. Kong, K. Yu, R. Wang, H. Chen, H. Guo, J. Yan, K.A. Cunningham, Y. Chang, T. Liu, K.W. Williams, Cell Rep. 18 (2017) 583-592.

[10] A.C. Anithaaa, K. Asokanb, C. Sekara, Sensor. Actuator. B Chem. 238 (2017) 667-675.

[11] C.E.V. Ewijk, G.E. Jacobs, A.R.J. Girbes, Ann. Intensive Care 6 (2016) 85-92.

[12] A. Fricka, F. Ahsa, L. Appelc, M. Jonassonc, K. Wahlstedta, M. Banid, E.M. Pichd,P. Betticad, B. Langstrome, M. Lubberinkc, M. Fredriksona, T. Furmark, Eur. Neuropsychopharmacol 26 (2016) 1775-1783.

[13] O. Jha, R.A. Yadav, J. Mol. Struct. 1123 (2016) 92-110.

[14] V. Mukherjee, N.P. Singh, R.A. Yadav, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 107 (2013) 46-54.

[15] P. Song, X. Guo, Y. Pan, Y. Wen, Z. Zhang, H. Yang, J. Electroanal. Chem. 688 (2013) 384-391.

[16] E. Ozdemir, Int. J. Basic Clin. Pharmacol. 6 (2017) 217-228.

[17] O. Jha, T.K. Yadav, R.A. Yadav, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 173 (2016) 307-317.

[18] J. Pratuangdejkul, W. Nosoongnoen, G.A. Guerin, S. Loric, M. Conti, J.M. Launay,P. Manivet, Chem. Phys. Lett. 420 (2006) 538-544.

[19] L.F. Pisterzi, D.R.P. Almeida, G.A. Chass, L.L. Torday, J.G. Papp, A. Varro,
I.G. Csizmadia, Chem. Phys. Lett. 365 (2002) 542-551.

[20] T.V. Mourik, L.E.V. Emson, Phys. Chem. Chem. Phys. 4 (2002) 5863-5871.

[21]A. Lagutschenkov, J. Langer, G. Berden, J. Oomens, O. Dopfer, J. Phys. Chem. A 114 (2010) 13268e13276.

[22]T.A. LeGreve, E.E. Baquero, T.S. Zwier, J. Am. Chem. Soc. 129 (2007) 4028-4038.

[23] T.M. Kolev, B.A. Stamboliyska, Spectrochim. Acta A 56 (1999) 119-126.

[24]V. Krishnakumar, V. Balachandran, Spectrochim. Acta A 61 (2005) 1181-1186.

[25]C.P. Dwivedi, S.N. Sharma, Indian J. Pure Appl. Phys. 11 (1973) 447e451.

[26]V. Krishnakumar, R.J. Xavier, Indian J. Pure Appl. Phys. 41 (2003) 597-601.

[27] S. Gunasekaran, R.T. Kumar, S. Ponnusamy, Spectrochim. Acta, Part A A. 65 (2006) 1041-1052.

[28] N.B. Colthup, L.H. Daly, S.E. Wiberly, Introduction to Infrared and Raman Spectroscopy, Academic press, Newyork, 1990.

[29] D.N. Sathyanarayana, Vibrational Spectroscopy Theory and Applications, New Age International Publishers, New Delhi, 2004.

[30] V. Pouchaname, R. Madivanane, A. Tinabaye, K.B. Santhi, Struct. Chem. Com- mun. 2 (2011) 129-143.

[31] Y.X. Zhao, X.Y. Sun, Spectroscopic Identification of Organic Structures, Science Press, 2010.

[32] C. Andraud, T. Brotin, C. Garcia, F. Pelle, P. Goldner, B. Bigot, A. Collet, J. Am. Chem. Soc. 116 (1994) 2094-2102.

[33] A.J.A. Bienko, Z. Latajka, D.C. Bienko, D. Michalska, Chem. Phys. 250 (1999) 123-294.

[34] V.M. Geskin, C. Lambert, J.L. bredas, J. Am. Chem. Soc. 125 (2003) 15651-15658.

[35] N. Sundaraganesan, H. Saleem, S. Mohan, M. Ramalingam, V. Sethuraman, Spectrochim. Acta, Part A 62 (2005) 740-751.

[36] D. Mamad, N. Bulut,J. Phy. chem. &functional martials 2652-3080.

[37]M. M. Borah, Th. Gomti Devi, J. Molecular structure,1161(2018) 464- 476.