Volume 9, Issue 2, 2020, 1079 - 1082 **ISSN 2284-6808**

Letters in Applied NanoBioScience

https://nanobioletters.com/

https://doi.org/10.33263/LIANBS92.10791082

Original Research Article **Open Access Journal**

Received: 01.04.2020 / Revised: 03.05.2020 / Accepted: 04.05.2020 / Published on-line: 10.05.2020

Computational notes on the electronic properties of carboxylic acid

Asmaa Ibrahim [1], Hanan Elhaes [1], Medhat Ibrahim [2,*]

[1] Physics Department, Faculty of Women for Arts, Science and Education, Ain Shams University, 11757 Cairo, Egypt

[2] Molecular Spectroscopy and Modeling Unit, Spectroscopy Department, National Research Centre, 33 El-Bohouth St., 12622 Dokki, Giza, Egypt

*corresponding author e-mail address: ***medahmed6@yahoo.com*** | Scopus ID 8641587100

ABSTRACT

The present work describing the electronic properties and vibrational characteristics of carboxylic acids. Acetic acid is chosen as model molecules then optimized at B3LYP/6-31g(d,p) level of theory. The vibrational frequencies were calculated at the same level of theory. Band assignments which were calculated as 18 normal modes were assigned as one compare the normal mode coordinates with original one. Band assignments were described indicating the directions of normal modes in terms the vibrating atoms of the acetic acids. It could be concluded that DFT could be a useful tool for elucidation both the structural and vibrational features of carboxylic acids and then further utilized for assignment of the structures contains carboxyl groups which are known as most reactive structures in chemistry, biology and environment.

Keywords: *Acetic acids; DFT; Normal mode and IR assignment.*

1. INTRODUCTION

Functional groups are leading the chemical interaction according to the role of their hydrogen bonding that they own. Carboxyl group among the most common reactive functional groups [1-4]. It is stated that carboxyl group is among the most reactive functional groups and plays an important role in many interactions specially in chemistry, biology and environment [5-8]. Structure containing carboxyl group is really leading the chemical as well as biological interactions [9-10]. In this sense understanding, the structural and vibrational characteristics of carboxyl group is a point of research interest in both experimental and theoretical basis [11-13].

Accordingly, density functional theory, as well as ab initio quantum mechanical calculations, are utilized to understand carboxyl group as well as structures containing carboxyl group [14-18].

It is stated that a different class of molecular modeling could be utilized to investigate physical, chemical and thermal properties of many structures and molecules whereas the experimental data are limited or even unavailable [19-24].

Based on these considerations the present study is conducted as computational notes to optimized carboxylic acid then assign the vibrational characteristics. Acetic acids were chosen as a model molecules then geometrical parameters are indicated graphically then each normal mode was indicated by arrows upon the atoms of acetic acid to describe graphically the 18 normal of acetic acid model molecule.

2. MATERIALS AND METHODS

Calculations Details.

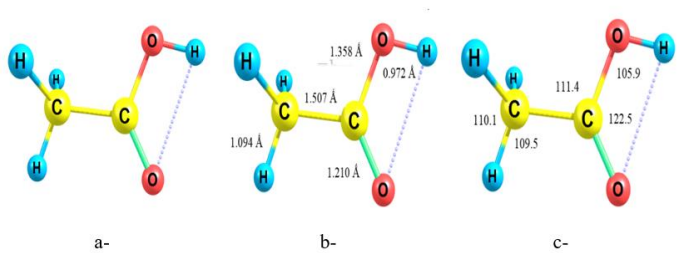
Acetic acid was chosen as a model molecule for carboxylic acids then it was calculated with Gaussian 09 [25] softcode at spectroscopy Department, National Research Centre. Structures were optimized at density functional theory DFT:B3LYP/6-31g(d,p) [26-28], the vibrational spectra were calculated at the same level of theory.

3. RESULTS

Acetic acid which indicated in figure 1-a, was optimized at DFT:B3LYP/6-31g(d,p) level. The optimized structures indicated the calculated bond distances as shown in figure 1-b, while the bond angles are indicated in figure 1-c.

Vibrational spectra were calculated at the same level of theory. The assignment of each normal mode is indicated both in table 1 and figures 2-1 to 2-18. The structure of acetic acid contains 8 atoms so that it is expected to have 18 normal modes (3x8-6=18) which already assigned in table 1 and indicate graphically as in figure 2.

The band assignment is aided by the computer software in which the coordinates of each normal mode is compared with the coordinates of the normal coordinates before vibration.



a- b- c-

Figure 1. B3LYP/6-31g(d,p) calculated the optimized structure of a-acetic acid, b-acetic acid structure indicating bond distance, c- acetic acid structure indicating bond angles.

The HOMO/LUMO band gap energy as indicated in table 2 is calculated as 7.756 eV while the total dipole moment was 1.605 Debye. Figure 3-a presents the mapped HOMO/LUMO orbitals

which calculated also at the same level of theory. Finally, at figure 3-b indicates the contour of the molecular electrostatic potential MESP for acetic acid.

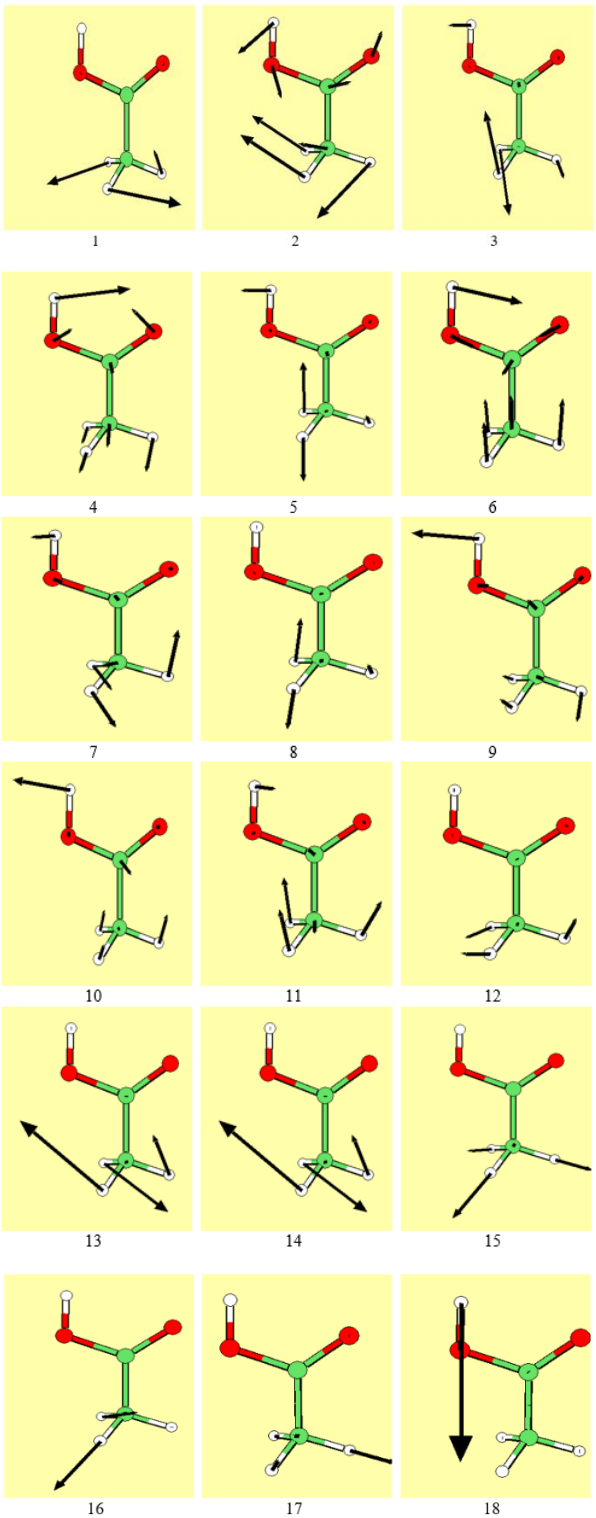


Figure 2. Band assignment for the 18 normal modes of the studied acetic acid which was calculated at B3LYP/6-31g(d,p) level of theory.

Table 1. B3LYP/6-31g(d,p) calculated frequencies for acetic acid followed by the band assignment.

Normal Mode	IR Frequency	Band Assignment
1	69.1472	CH3 torsion
2	419.8942	C-OH torsion
3	542.5553	CCO deform
4	581.7181	C=O op-bend
5	681.6924	OCO deform
6	865.7887	C-C stretch
7	1002.3652	CH3 rock
8	1069.9052	CH3 rock
9	1216.3154	C-O stertch
10	1355.3911	OB bend
11	1422.5017	CH3 s-stretch
12	1484.2944	CH3 d-deform
13	1489.8154	CH3 d-deform
14	1855.7454	C=O stretch
15	3067.9577	CH3 s-stretch
16	3133.5925	CH3 d-stretch
17	3186.1694	CH3 d-stretch
18	3754.1293	OH-stretch

Table 2. Calculated B3LYP/6-31g(d,p) for HOMO/LUMO band gap energy as eV and total dipole moment TDM as Debye.

Physical Quantity	ΔE	TDM
Calculated Value	7.756	1.605

MESP is an important physical quantity represents the charge distribution for acetic acid. It is stated that both MESP and TDM beside HOMO/LUMO band gap energy are reflecting the reactivity of the given structure [29-31]. MESP is necessary for understanding the electrophilic and nucleophilic attacks sites for acetic acid [32] it is mapped by colors in which the potential is following the increasing orders: red < orange < yellow < green < blue.

The blue indicates the highest MESP and the red indicates the lowest MESP [33].

The present computational notes indicated the suitability of the density functional theory DFT:B3LYP/6-31g(d,p) to study geometrical, vibrational as well as a physical parameter of carboxylic acids and structures containing carboxyl group.

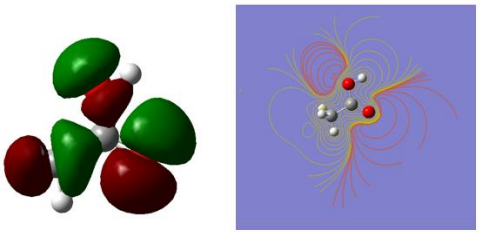


Figure 3. Calculated B3LYP/6-31g(d,p) for a- HOMO/LUMO acetic acid, b- Molecular electrostatic potential MESP contour of acetic acid.

4. CONCLUSIONS

DFT level of theory is an important computational tool for studying organic structures with reactive functional groups like carboxyl. The importance of this structure is that it is important in many areas as it could connect metals with organic structures through hydrogen bonding. It could be concluded that computational methods are used to study physical, chemical and biological interaction and provides important information about structural and vibrational characteristics. This work is confirming the previous findings [34-39].

5. REFERENCES

1. Smith, D.A.; Wallwork, M.L.; Zhang, J.; Kirkham, J.; Robinson, C.; Marsh, A.; Wong, M. The Effect of Electrolyte Concentration on the Chemical Force Titration Behavior of ω-Functionalized SAMs: Evidence for the Formation of Strong Ionic Hydrogen Bonds. *The Journal of Physical Chemistry B* **2000**, *104*, 8862-8870, https://doi.org/10.1021/jp0023056.
2. Kokkoli, E.; Zukoski, C.F. Surface Pattern Recognition by a Colloidal Particle. *Langmuir* **2001**, *17*, 369-376,https://doi.org/10.1021/la0006059.
3. Boubour, E.; Lennox, R.B. Insulating Properties of Self-Assembled Monolayers Monitored by Impedance Spectroscopy. *Langmuir* **2000**, *16*, 4222-4228,https://doi.org/10.1021/la991328c.
4. Sugihara, K.; Shimazu, K.; Uosaki, K. Electrode Potential Effect on the Surface pKa of a Self-Assembled 15-Mercaptohexadecanoic Acid Monolayer on a Gold/Quartz Crystal Microbalance Electrode. *Langmuir* **2000**, *16*, 7101-7105,https://doi.org/10.1021/la991301t.
5. Franco, M.; Nealey, P.F.; Campbell, S.; Teixeira, A.I.; Murphy, C.J. Adhesion and proliferation of corneal epithelial cells on self-assembled monolayers. *Journal of Biomedical Materials Research* **2000**, *52*, 261-269,https://doi.org/10.1002/1097-4636(200011)52:2<261::AID-JBM4>3.0.CO;2-2.
6. Chapman, R.G.; Ostuni, E.; Yan, L.; Whitesides, G.M. Preparation of Mixed Self-Assembled Monolayers (SAMs) That Resist Adsorption of Proteins Using the Reaction of Amines with a SAM That Presents Interchain Carboxylic Anhydride Groups. *Langmuir* **2000**, *16*, 6927-6936, https://doi.org/10.1021/la991579l.
7. MacCarthy, P.; Suffet, I.H. *Aquatic humic substances and their influence on the fate and treatment of pollutants*. 1989; pp. R17-R30.
8. Livens, F.R. Chemical reactions of metals with humic material. *Environmental Pollution* **1991**, *70*, 183-208, https://doi.org/10.1016/0269-7491(91)90009-L.
9. Pandey, A.K.; Pandey, S.D.; Misra, V. Stability Constants of Metal–Humic Acid Complexes and Its Role in Environmental Detoxification. *Ecotoxicology and Environmental Safety* **2000**, *47*, 195-200, https://doi.org/10.1006/eesa.2000.1947.
10. Tsutsuki, K.; Kuwatsuka, S. Chemical studies on soil humic acids. *Soil Science and Plant Nutrition* **1978**, *24*, 547-560,https://doi.org/10.1080/00380768.1978.10433134.
11. Badry, R.; Omar, A.; Mohammed, H.; Mohamed, D.A.A.; HananElhaes; Refaat, A.; Ibrahim, M. Effect of Alkaline Elements on the Structure and Electronic properties of Glycine. *Biointerface research in applied chemistry* **2018**, *8*, 3682-3687.
12. Badry, R.; Ghanem, A.S.; Ahmed, H.; Fahmy, A.; Elhaes, H.; Refaat, A.; Ibrahim, M. Effect of Li, Na, K, Be, Mg and Ca on the electronic properties, geometrical parameters of carboxylic acids. *Biointerface research in applied chemistry* **2018**, *8*, 3657-3660.
13. Bayoumy, A.M.; Badry, R.; Gaber, H.A.; Elbiomy, S.A.; El Gabaly, S.G.; Abd ElAziz, M.S.; Gouda, S.M.; Elhaes, H.; Yahia, I.S.; Zahran, H.Y.; Ibrahim, M. Molecular modeling analyses for the effect of solvents on amino acids.*Biointerface Research in Applied Chemistry***2019**, *9*, 4379-4383.
14. Foresman, J.B.; Frisch, A. Chapter 1-Computational models and model chemistry.In: *Exploring chemistry with electronic structure methods.*2nd ed., Gaussian Inc. 1996.
15. Hehre, W.J.; Radom, L.; Schleyer, P.V.R.; Pople, J.A.*Ab initio Molecular Orbital Theory*. Wiley, New York 1986.
16. Foresman, J.B. Ab initio techniques in chemistry: interpretation and visualization. In: *What Every Chemist Should Know About Computing.*Acs Books, Washington, D.C. 1996.
17. Ezzat, H.A.; Hegazy, M.A.; Nada, N.A.; Ibrahim, M.A. Effect of Nano Metal Oxides on the Electronic Properties of Cellulose, Chitosan and Sodium Alginate. *Biointerface Research in Applied***2019**, *9*, 4143-4149.
18. Bayoumy, A.M.; Elhaes, H.; Osman, O.; Hussein, T.; Ibrahim, M.A. Mapping Molecular Electrostatic Potential for Heme Interacting with Nano Metal Oxides.*Biointerface Research in Applied Chemistry***2020,***10*, 5091–5095.
19. Ghashghaee, M.; Azizi, Z.; Ghambarian, M. Conductivity tuning of charged triazine and heptazine graphitic carbon nitride (g-C3N4) quantum dots via nonmetal (B, O, S, P) doping: DFT calculations. *Journal of Physics and Chemistry of Solids* **2020**, *141*, https://doi.org/10.1016/j.jpcs.2020.109422.
20. Mohammadi-rad, N.; Esrafili, M.D.; Sardroodi, J.J. CuN3 doped graphene as an active electrocatalyst for oxygen reduction reaction in fuel cells: A DFT study. *Journal of Molecular Graphics and Modelling* **2020**, *96*, https://doi.org/10.1016/j.jmgm.2020.107537.
21. Singh, S.; Kaur, I. Bandgap engineering in armchair graphene nanoribbon of zigzag-armchair-zigzag based Nano-FET: A DFT investigation. *Physica E: Low-dimensional Systems and Nanostructures* **2020**, *118*, https://doi.org/10.1016/j.physe.2020.113960.
22. Mofidi, F.; Reisi-Vanani, A. Investigation of the electronic and structural properties of graphyne oxide toward CO, CO2 and NH3 adsorption: A DFT and MD study. *Applied Surface Science* **2020**, *507*, 145134, https://doi.org/10.1016/j.apsusc.2019.145134
23. Abdelsalam, H.; Saroka, V.A.; Ali, M.; Teleb, N.H.; Elhaes, H.; Ibrahim, M.A. Stability and electronic properties of edge functionalized silicene quantum dots: A first principles study. *Physica E: Low-dimensional Systems and Nanostructures* **2019**, *108*, 339-346,https://doi.org/10.1016/j.physe.2018.07.022.
24. Grenni, P.; Caracciolo, A.B.; Mariani, L.; Cardoni, M.; Riccucci, C.; Elhaes, H.; Ibrahim, M.A. Effectiveness of a new green technology for metal removal from contaminated water. *Microchemical Journal* **2019**, *147*, 1010-1020, https://doi.org/10.1016/j.microc.2019.04.026.
25. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A. Gaussian09, revisions D. 01 and B. 01; Gaussian, Inc. *Wallingford, CT* **2010**.
26. Becke, A.D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.***1993**, *98*, 5648–5652, https://doi.org/10.1063/1.464913..
27. Lee, C.; Yang, W.; Parr, R.G. Development of the Colic-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B***1988**, *37*, 785, https://doi.org/10.1103/PhysRevB.37.785.
28. Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results Obtained with the Correlation Energy Density Functionals of Becke and Lee, Yang and Parr. *Chem. Phys. Lett*. **1989**, *157*, 200–206,https://doi.org/10.1016/0009-2614(89)87234-3.
29. Ibrahim, M.; El-Haes, H. Computational Spectroscopic Study of Copper, Cadmium, Lead and Zinc Interactions in the Environment. *Int. J. Environ. Pollut.***2005,***23*, 417-424, http://dx.doi.org/10.1504/IJEP.2005.007604.
30. brahim, M.; Mahmoud, A.A. Computational Notes on the Reactivity of Some Functional Groups. *Journal of Computational*

and Theoretical Nanoscience **2009**, *6*, 1523-1526,https://doi.org/10.1166/jctn.2009.1205.
31. Politzer, P.; Murray, J.S.; Sen, K.D. Molecular electrostatic potentials: concepts and applications. *J. Theor. Comput. Chem* **1996**, *3*, 27.
32. Politzer, P.; Laurence, P.R.; Jayasuriya, K. Molecular electrostatic potentials: an effective tool for the elucidation of biochemical phenomena. *Environ. Health Persp.* **1985**, *61*, 191-202, https://doi.org/10.1289/ehp.8561191.
33. Şahin, Z.S.; Şenöz, H.I.; Tezcan, H.; Büyükgüngör, O. Synthesis, spectral analysis, structural elucidation and quantum chemical studies of (E)-methyl-4-[(2-phenylhydrazono)methyl]benzoate. *Spectrochim. Acta A* **2015**, *143*, 91-100, https://doi.org/10.1016/j.saa.2015.02.032.
34. Liu, Y.; Peng, Y.; An, B.; Li, L.; Liu, Y. Effect of molecular structure on the adsorption affinity of sulfonamides onto CNTs: Batch experiments and DFT calculations. *Chemosphere* **2020**, *246*, https://doi.org/10.1016/j.chemosphere.2019.125778.
35. Mollania, F.; Hadipour, N.L.; Mollania, N. CNT-based nanocarrier loaded with pyrimethamine for adipose mesenchymal stem cells differentiation and cancer treatment: The computational and experimental methods. *Journal of Biotechnology* **2020**, *308*, 40-55, https://doi.org/10.1016/j.jbiotec.2019.11.005.
36. Ibrahim, M. Mapping the molecular electrostatic potential of fullerene. *Egyptian Journal of Chemistry* **2019**, *62*, 1391-1402, https://doi.org/10.21608/ejchem.2019.5353.1472.
37. Nematov, D.D.; Burhonzoda, A.S.; Khusenov, M.A.; Kholmurodov, K.T.; Ibrahim, M.A.A. The Quantum-Chemistry Calculations of Electronic Structure of Boron Nitride Nanocrystals with Density Functional Theory Realization. *Egyptian Journal of Chemistry* **2019**, *62*, 21-27, https://dx.doi.org/10.21608/ejchem.2019.12879.1805.
38. El Gabaly, S.G.; Youssif, G.M.;Bayoumy, A.M.; Ezzat, H.; Elhaes, H.; Refaat, A.; Ibrahim, M.A. Modeling The Effect of Functional Groups on The Electronic Properties of Benzene, Pyridine and Pyrimidine.*Egyptian Journal of Chemistry, Special issue, the First International Conference on Molecular Modeling and Spectroscopy***2019**, 1-11.
39. Doroshkevich, O.; Nabiev, A.A.; Shylo, A.; Pawlukojć, A.; Doroshkevich, V.S.; Glazunova, V.A.; Zelenyak, T.Y.; Doroshkevich, N.; Rahmonov, K.R.; Khamzin, E.K.; Nematov, D.D.; Burhonzoda, A.S.; Khusenov, M.; Kholmurodov, K.; Majumder, S.; Balasoiu, M.; Madadzada, A.; Bodnarchuk, V.I. Frequency modulation of the Raman spectrum at the interface DNA - ZrO2 nanoparticles. *Egyptian Journal of Chemistry* **2019**, *62*, 13-15, https://doi.org/10.21608/ejchem.2019.12898.1806.