Journal of Physical Chemistry and Functional Materials Volume 6, Issue 1 (2023) 77-82

Journal of Physical Chemistry and Functional Materials

Home Page of Journal: https://dergipark.org.tr/jphcfum

Investigation of Electronic and Spectroscopic Properties of Ca-Phosphosilicate molecule by Quantum Programming

Mehmet Hanifi Kebiroğlu

Malatya Turgut Özal University, Darende Bekir Ilıcak Vocational School, Opticianry Program, 44700, Malatya, Türkiye
** Corresponding author: E-mail: hanifi007@hotmail.com*

ABSTRACT

Computational chemistry methods were used to explore the molecular and atomic characteristics of the Ca-Phosphosilicate molecule, known as BioGlass. In this spectroscopic investigation, the active portions of the molecule were calculated using the Hartree-Fock (HF) technique with the STO-3G basic set, the HOMO-LUMO energy range, and the electrophilic and nucleophilic regions with Frontier Molecular Orbital Analysis (FMO)que with the STO-3G basic set, the HOMO-LUMO energy range, and the electrophilic and nucleophilic regions with Frontier Molecular Orbital Analysis (FMO). The Fourier transform infrared (FTIR) spectroscopic technique was used to compute IR and FT-Raman. The structure of the molecules was established using nuclear magnetic resonance spectra. UV spectroscopy was used to establish the structure's region. The transition rates of density of state (DOS) were calculated. The charge distribution and molecular electrostatic potential (MEP) of a molecular system were identified.

ARTICLE INFO

Keywords:

HF
HOMO
LUMO
DOS
Ca-Phosphosilicate

Received: 2023-04-28
Accepted: 2023-06-02
ISSN: 2651-3080
DOI: 10.54565/jphcfum.1289545

Introduction

A Ca-Phosphosilicate bioactive glass (BioGlass) system may initiate ion exchange processes in an aqueous solution to produce carbonated hydroxyapatite, a mineral that mimics tooth enamel. As hydrogen ions replace sodium particles in the formulation, the pH rises. Calcium and Phosphosilicate ions can be released within a few days, and this combination can subsequently crystallize into hydroxycarbonate apatite, forming a thin coating of calcium- Phosphosilicate -rich material on tooth surfaces. While the term "bioactivity" should be defined, bioactive glass materials are widely used in clinical dentistry. Dental materials that are biologically active or have a biological purpose can interface with strong tissues like dentin and enamel either chemically or physically [1-5]. The aim of this study is to investigate the structural and electronic properties of Phosphosilicate molecule by adding Ca atom [6].

Methods

Since it became computationally feasible to solve HF equations in the 1960s as a result of pioneering work by Frose-Fischer, Brage, Johnsson, Hibbert, and others in post-HF approaches like HF and Multi-HF, programs for doing so have been developed. Configuration Interaction between Hartree-Fock and configuration the radial grating-based solver is one of the notable codes created specifically for the HF atomic structure. There is just one generally accessible code that uses B-splines to solve HF equations. Dirac can be solved by software, and Fock's equations have also been made public. The B-spline provides an efficient way to encompass the energy continuum and provides rapid convergence in sums across intermediate states including energy denominators in multibody computations, therefore the problem can be solved in this way [6]. Its entire structural configuration has been optimized for singlet electronic states with the ground state method and STO-3G theory level. It was done using Gaussian 09 W for electronic structure calculations and Gauss View 5.0.9 for structural visualization [7,8].

Results and Discussion

Optimized Geometry

Quantum chemical calculations were performed to optimize the Ca-phosphosilicate molecule utilizing the Gaussian 09 W computer package's STO-3G-based HF approach [7]. Figure 1 depicts the optimal structure of the Ca-phosphosilicate compound. Figure 2 depicts the optimization energy profile and bias targets of Ca-phosphosilicate. The essential optimization phases are colored in the HF optimization energy profile (Figure 2): blue for the first optimization step, green for additional optimization steps, and red for the final optimization step.

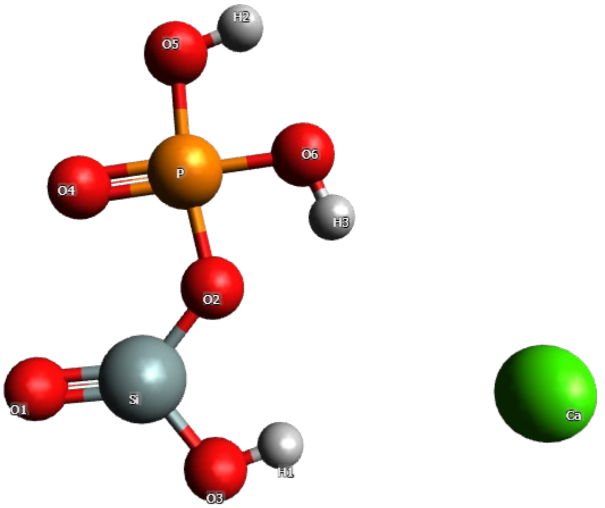

Figure 1. Optimize structure of Ca-Phosphosilicate molecule

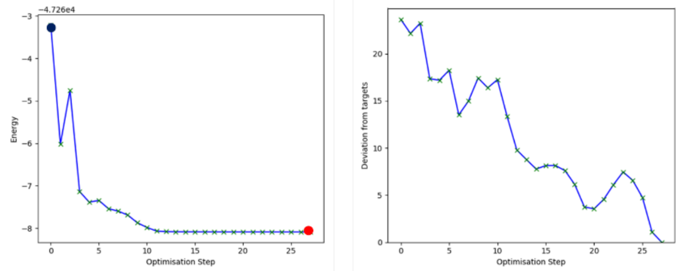

Figure 2. Optimization energy profile and deviation targets of Ca-Phosphosilicate

HOMO-LUMO and Electronic Density of States (DOS) Analysis

The wave function analysis reveals that electron absorption relates to the transition from the ground state to the first excited state and is primarily characterized by the excitation of an electron from the highest occupied molecular orbital (HOMO) to the lowest empty orbital (LUMO). The energy level diagram of Ca-Phosphosilicate and the HOMO-LUMO structure is shown in Figure 3. The HOMO energy gap is -4.485 eV, the LUMO energy gap is 4.776 eV, and the Eg energy gap is 9.261 eV. The energy gaps between HOMO and LUMO explain the eventual charge transfer interactions that occur within the molecule [9].

Quantum mechanical studies give information on the behavior of electrons in metals, and first-principle HF calculations are effective strategies for increasing metal electronic DOS. Because of the complexity of multibody systems, quantum mechanics approaches have a significant computational burdenons are effective strategies for increasing metal electronic DOS. Because of the complexity of multibody systems, quantum mechanics approaches have a significant computational burden. As a result, it is a quick approach for many researchers to accurately forecast the electrical structures of materials. The HOMO-LUMO energy range of the acrylic acid molecule is shown in Figure 4's DOS calculation. The increased interaction energy of the acrylic acid molecule indicates that the interacting system is thermodynamically favorable [10].

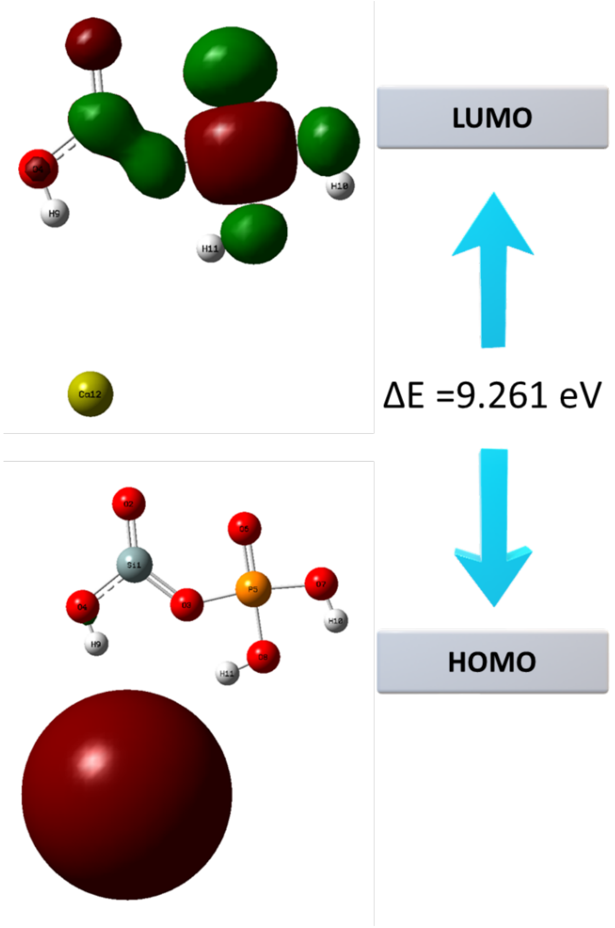

Figure 3. HOMO-LUMO structure with the energy level diagram of Ca-Phosphosilicate

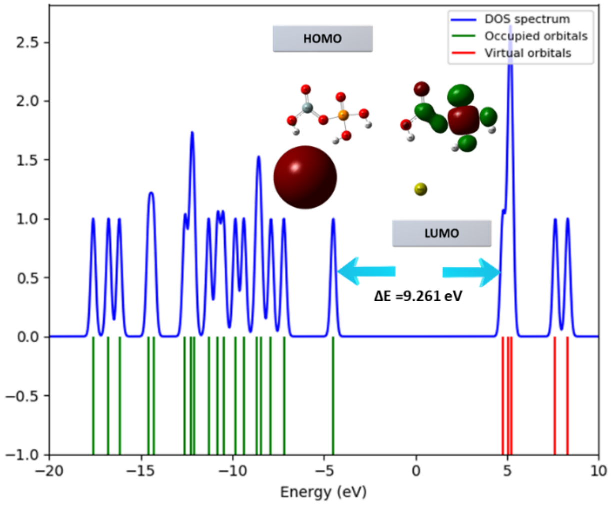

Figure 4. HOMO-LUMO structure with the energy level diagram and the density of states (DOS) with the contribution of Ca-Phosphosilicate

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy is an analytical method used to describe a biochemical profile and produce a unique molecular fingerprint. It offers significant advantages when paired with FTIR spectroscopy and machine learning [11].

It depicts the estimated FT-IR spectra of the examined molecule in the 4500 cm^{-1} to 0 cm^{-1} region. Displays absorption peaks. The frequencies in Figure 5 are harmonic frequencies. Harmonic frequencies are computed by multiplying the harmonic frequencies by the measurement factor applicable for each calculation level.

Complex similarity implies similarity in both spectrum and vibrational frequencies. The vibrational frequency of a bond increases as the bond strength grows and the mass of the bond atom decreases, according to the basic principles of vibrational spectroscopy. Figure 5 shows the maximum intensity at peak number 25, with a frequency of 1390 cm^{-1}. Other permeability values, including the peak values of 69, 54, 78, and 61, were somewhat altered. It shows the energy range between peak numbers 69 and 25 as 1390 cm^{-1} to 4270 cm^{-1}.

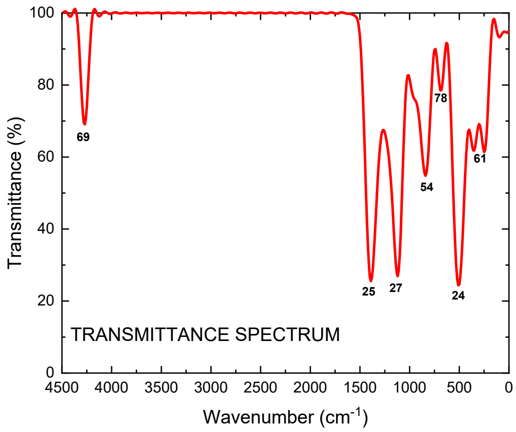

Figure 5. FT-IR spectrum of Ca-Phosphosilicate

Raman Spectrum

Raman spectroscopy is one of the most often utilized vibrational spectroscopy methods in pharmaceutical investigation due to its ease of sample preparation and solvent selection, as well as its high sensitivity and specificity. With the advancement of Raman spectroscopy, its applications in the identification of raw materials and formulations, drug susceptibility and microbiological testing, identifying illegal drugs, and screening pharmaceuticals have pushed the detection limits to extremely low concentrations [12]. Ca-Phosphosilicate's FT-Raman spectrum was acquired utilizing wavelengths ranging from 0 cm^{-1} to 1400 cm^{-1}. Figure 6 depicts the FT-Raman spectrum.

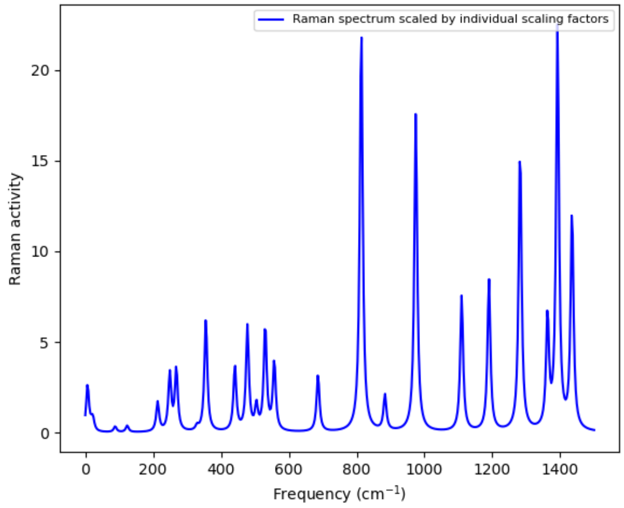

Figure 6. Raman Activity of Ca-Phosphosilicate

Nuclear Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance (NMR) is one of the analytical approaches to the Ca-phosphosilicate molecule [13]. NMR spectroscopy, or nuclear magnetic resonance, employs radiofrequency waves to expose information about magnetic nuclei. Because the term "spectroscopy" refers to any technique that uses electromagnetic (EM) radiation to probe atoms, NMR spectroscopy is just one of many spectroscopic methods used in everyday biology [14]. Table 1 shows the calculated chemical shift values. The peaks in the complex spectra that remain constant or move to higher regions are a significant indication that describes both the complexation and the atoms involved in the coordination. Because proton nuclei are highly shielded by their electrons, they peak at low ppmexes. Whether the peaks remain the same or shift to higher areas is an important indicator that explains both the complexation and the atoms involved in the coordination. Because proton nuclei are highly shielded by their electrons, they peak at low ppm. It produced eight peaks when evaluated in Figure 7.

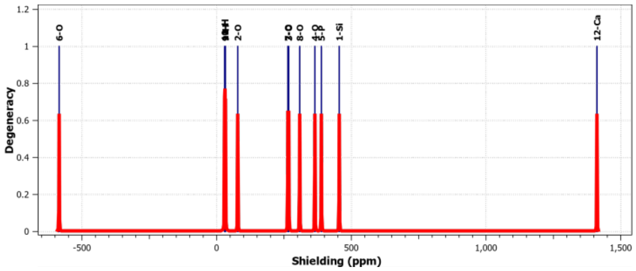

Figure 7. NMR spectrum of Ca-Phosphosilicate

Table 1. Chemical shifts of Ca-Phosphosilicate

Method	Shielding (ppm)
6-O	-584.6
10-H	29.6543
11-H	31.0463
9-H	32.5534
2-O	78.2552
7-O	264.4976
3-O	267.589
8-O	308.2728
4-O	364.7433
5-P	388.7562
1-Si	455.185
12-Ca	1411.714

UV–Visible Analysis

Chemists most likely found atomic structure and then molecule structure using UV-visible spectroscopy. Optical technologies, on the other hand, have made it simpler to examine the optical and electrical characteristics of nanoscale particles. Figure 8 depicts the absorbance spectra and peak of the HF/STO-3G Ca-Phosphosilicate structure. Because this absorption is visible and occurs in this region, the 390 nm peak indicates the color of the structure. The highest energy at 390 nm is 9.261 eV.

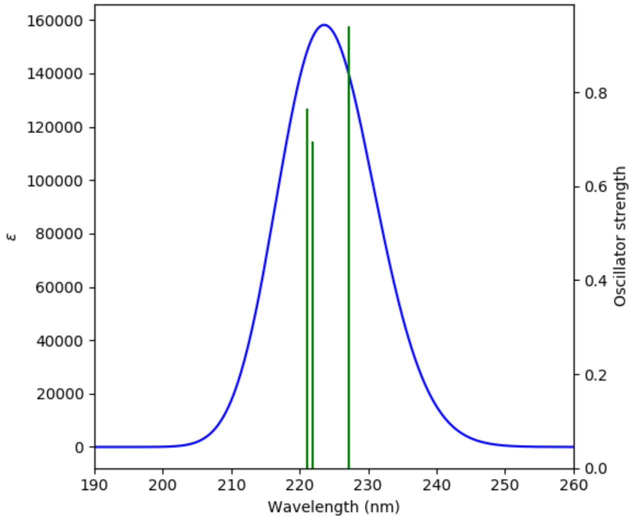

Figure 8. UV-visible absorption spectrum of Ca-Phosphosilicate

Molecular Electrostatic Potential (MEP) Surface

The Molecular Electrostatic Potential (MEP) Surface Analysis is one approach that might be beneficial in the design of linear receptors. For more than three decades, scientific research has logically used molecular electrostatic potential (MEP) maps. GaussView 5.0.9 software was used to uncover the surface analysis of the Molecular Electrostatic Potential (MEP) [15, 16]. On the molecular electrostatic potential surface, the charge distributions of molecules are shown in three dimensions. These surface investigations allow us to see the molecule's variably charged regions. Figure 9 depicts the Ca-Phosphosilicate Molecular Electrostatic Potential (MEP) surface [17–19].

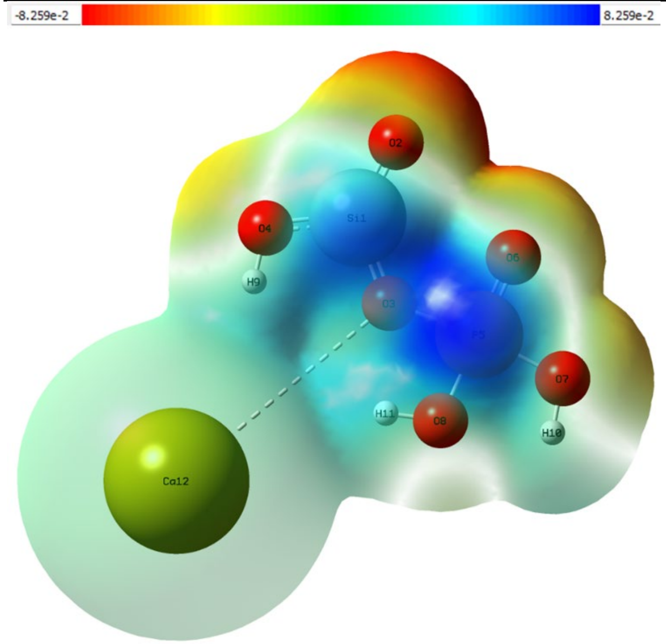

Figure 9. Molecular Electrostatic Potential of Ca-Phosphosilicate

Conclusion

To analyze the chemical and physical features of the Ca-Phosphosilicate molecule, quantum computational and spectroscopic vibrational studies were done. The FTIR and UV-Vis measurements of the molecule were compared to theoretical values obtained using the HF approach with the STO-3G basis set. The Ca atom had the greatest amount of HOMO energy. In LUMO, it was predominantly detected in P and Si atoms. Eg = 9.261 eV for HOMO-LUMO energy gaps, E_{HOMO} = -4.485 eV, and E_{LUMO} = 4.776 eV, indicating charge transfer. Fourier transform infrared (FT-IR) spectroscopy has a frequency of 1390 cm^{-1} with absorption peaks and maximum intensity at peak number 25. Other permeability values were slightly altered, including the peak values of 69, 54, 78, and 61. The energy range between peak numbers 69 and 25 is shown as 1390 cm^{-1} to 4270 cm^{-1}. The absorbance spectra and peak of the Ca-Phosphosilicate structure are studied using UV-visible spectroscopy. This absorption is apparent and happens in this area; the structure's color is shown by the 390 nm peak. At 390 nm, the highest energy is 9,261 eV. The HOMO-LUMO energy gap, state density (DOS) calculation, and growing interaction energy of the Ca-Phosphosilicate molecule all indicated that the interacting system is thermodynamically beneficial. The MEP map revealed that electron-rich areas and less-rich regions were colored from red to blue. Changing the alkyl chain of the Ca-Phosphosilicate molecule has little effect on its chemical activity, but it has a significant impact on its biochemical and biological activity. It has been seen in quantum chemical calculations that the energy is better when a Ca atom is added to the phosphosilicate molecule. The reason for the selection of the Ca atom is that it is suitable for the structure.

References

[1] Wefel, J.S., (2009). NovaMin: likely clinical success. Adv. Dent. Res. 21, 40-43.

[2] Vallittu, P., Boccaccini, A., Hupa, L., Watts, D., (2018). Bioactive dental materials Do they exist and what does bioactivity mean? Dent. Mater. 34, 693–694.

[3] Yoshimi Shioya and Mamoru Maeda (1986), Journal of The Electrochemical Society the Electrochemical Society, find out more Comparison of Phosphosilicate Glass Films Deposited by Three Different Chemical Vapor Deposition Methods, J. Electrochem. Soc. 133 1943

[4] L. R. Thompson, J. J. Rocca, K. Emery, P. K. Boyer, and G. J. Collins, (1983). "Electron beam assisted chemical vapor deposition of SiO2", Appl. Phys. Lett. 43, 777-779.

[5] Tóth, A.L., Puskás, J.É. (1980). Energy dispersive X-ray microanalysis of phosphosilicate glasses (PSG). Acta Physica 49, 133–140.

[6] Muz, İ. (2019). Structural And Electronıc Propertıes Of B6-Ncnhn (N=0-6) Serıes Upon The Substıtutıon Of Boron Atoms By The C-H Groups: A Densıty Functıonal Theory Study . Selçuk Üniversitesi Mühendislik, Bilim Ve Teknoloji Dergisi , 7 (2) , 467-477 . DOI: 10.15317/Scitech.2019.212

[7] Dennington R, Keith TA, Millam JM. (2009). GaussView 5.0.9

[8] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[9] Waide, D. T., Green, D. G., & Gribakin, G. F. (2020). BSHF: A program to solve the Hartree–Fock equations for arbitrary central potentials using a B-spline basis. Computer Physics Communications, 250, 107112. doi:10.1016/j.cpc.2019.107112.

[10] Shahab, S., Sheikhi, M., Filippovich, L., Anatol'evich, D. E., & Yahyaei, H. (2017). Quantum chemical modeling of new derivatives of (E,E)-azomethines: Synthesis, spectroscopic (FT-IR, UV/Vis, polarization) and

thermophysical investigations. Journal of Molecular Structure, 1137, 335–348. doi:10.1016/j.molstruc.2017.02.056

[11] Kavitha, E., Sundaraganesan, G., & Sebastian, S. (2010). Molecular structure, vibrational spectroscopic and HOMO, LUMO studies of 4-nitroaniline by density functional method. Indian Journal of Pure and Applied Physics, 48, 20–30.

[12] Yeo, B.C., Kim, D., Kim, C. et al. (2019). Pattern Learning Electronic Density of States. Sci Rep 9, 5879.

[13] Dou, J., Dawuti, W., Zheng, X., Zhu, Y., Lin, R., Lü, G., & Zhang, Y. (2023). Rapid discrimination of Brucellosis in sheep using serum Fourier transform infrared spectroscopy combined with PCA-LDA algorithm. Photodiagnosis and Photodynamic Therapy, 42, 103567.

[14] Shah, K. C., Shah, M. B., Solanki, S. J., Makwana, V. D., Sureja, D. K., Gajjar, A. K., … Dhameliya, T. M. (2023). Recent advancements and applications of Raman spectroscopy in pharmaceutical analysis. Journal of Molecular Structure, 1278, 134914.

[15] Naveen Kumar, M. S., Gupta, G., Kumar, V., Jagannathan, N. R., Sinha, S., Mewar, S., & Kumar, P. (2022). Differentiation between sepsis survivors and sepsis non-survivors through blood serum metabolomics: A proton nuclear magnetic resonance spectroscopy (NMR) study. Magnetic Resonance Imaging, 89, 49–57.

[16] Bothwell, J. H. F., & Griffin, J. L. (2011). An introduction to biological nuclear magnetic resonance spectroscopy. Biological Reviews, 86(2), 493–510.

[17] D. Sharma , S.N. Tiwari , (2016). Comparative computational analysis of electronic structure, MEP surface and vibrational assignments of a nematic liquid crystal: 4-n-methyl-4′-cyanobiphenyl J. Mol. Liq. 214 128–135.

[18] P. Politzer and J. S. Murray, (2017). σ-Hole Interactions: Perspectives and Misconceptions, Crystals 7, 212;

[19] J.M. Campanario , E. Bronchalo , M.A. Hidalgo, (1994). An Effective Approach for Teaching Intermolecular Interactions , J. Chem. Educ. 71 761–766 .