

DFT- HF and Experimental Calculation of the UV-Vis Absorption Spectra of Isonitrosoacetophenone INAP (C₈H₇NO₂)

Salma Fath Alrahman Ahmed¹

Khalid Mohammed Haroun¹

Abdalsakhi Suliman²

Adam Mohammed Adam Bakheet³

Yousif Hassan Alsheikh^{4,5}

¹Alzaeim Al-Azhari University, Bahry, Sudan

²University of Gezira, Madani Sudan

³AlNeenlen University, Khartoum, Sudan

⁴Omdurman Ahlia University, Omdurman, Sudan

⁵The Future University, Khartoum, Sudan

Abstract. The Density Functional Theory (DFT) and Hartree Fock (HF) Calculation has been performed for the fully optimized ground state structure of isonitrosoacetophenone (INAP) compound, to investigate the electronic absorption properties for INAP (C₈H₇NO₂). DFT and HF method were used along with (6-311g, 6-311g(d) and 6-311g (d,p) basis set for vertical excitation energy of electronic spectra. In addition, the UV-Vis results were obtained from the simulation using the Gaussian software employing DFT and HF method and experimental using a UV-Vis spectrometer device. The results of the two methods (DFT and HF) were compared with the experimental results, which show that the results of 10676 M.cm⁻¹ for experimental, 7500 M.cm⁻¹ for HF (basis set 6-311g) method basis set and 9100 M.cm⁻¹ for HF (basis set 6-311g (d) method basis set] for vertical excitation energy of electronic spectra. We find that HF (basis set 6-311g (d,p) method abstract agree for experimental results than the DFT method.

Key words: Gaussian view, DFT, HF, Isonitrosoacetophenone, absorption coefficient.

Introduction

The properties of the advanced solid materials made them very important and interesting for the technological point of view (Baseden and Tye, 2014: 2116-2123; Kaczmarek et al., 2019: 749-774). Two quantum mechanical *ab-initio* approaches commonly used in condensed matter are Hartree-Fock (HF) and Density functional theory (DFT) (Friesner, 2005: 6648-6653). Among these, DFT is used extensively for the study of bulk materials. One of the most promising solid materials is the isonitrosoacetophenone (C₈H₇NO₂) and is one of the most promising oximes with its wide range of applications (Sing, 2005: 789-796). Oximes are highly crystalline and very useful for purification and characterization of carbonyl compounds. It is also useful as efficient protecting groups for aldehydes and ketones (Sing, 2005: 789-796). The oximes have important analytical applications in the determinations of metal concentration from natural products. Some of these oxime ligands have catalytic and biological activities. Oximes and dioxides exhibit a broad range of pharmacological activity (Kaya et al., 2016: 52; Raut et al., 2011: 195-199). There is a need to study the absorption of the interesting isonitrosoacetophenone, the experimental methods to study this material including Fourier Transform Infrared Spectroscopy (FTIR) (Seshadri and Rasheed: 6-18), Raman

Spectroscopy, Nuclear Magnetic Resonance Spectroscopy (NMR) (Seshadri and Rasheed: 6-18), and UV-Vis spectroscopy (Lamsabhi et al., 2011: 1220-1230) and so on. In this article, the UV-Vis results were obtained from the simulation using the Gaussian software employing DFT and HF method and the results of the two methods were compared.

Gaussian software is capable of predicting many properties of molecules and reactions, including molecular energies and structures of transition states, bond and reaction energies, molecular orbitals, multi-pole moments, atomic charges and electrostatic potential, etc. Computation using Gaussian software can be carried out on many systems such as solutions, gas phase, both in their ground or in an excited state. Unless explicitly specified, RHF is used for singlets and UHF for higher multiplicities. In the latter case, separate α and β orbitals will be computed. RHF, ROHF or UHF can also be specified explicitly (Alama et al., 2018: 65-78). B3LYP is one of the energy functional of the density functional methods. The energy is reported in DFT calculations in a form similar to that of Hartree-Fock calculations. The quantum mechanical theory (DFT) is widely used in physics and chemistry aspects to study the electronic structure of many-body systems, particularly, atoms, molecules and the condensed phases. Therefore, DFT (Tosun, 2010: 65-74), is one of the most common and flexible methods which can be obtained in condensed matter physics, computational physics, and computational chemistry (Erdogdu et al., 2017: 553-563), due to its ability to deal with a complex system of electrons with high accuracy (Özmen, 2000: 67-79). Gauss View uses these constructs (Molecules, Molecule Groups and Views) to organize the many molecules which are being utilized at any given time (Frisch et al., 2009). In this study, the agreement between the experimental and calculated vibrational frequencies of isonitrosoacetophenone was investigated. The geometrical optimization and vibrational frequency calculations of the molecule were carried out by using *ab-initio* methods. 6-31G(d) and 6-311++G(d,p) basis sets were used with the DFT-B3LYP method and a 6-31 G(d) basis set was used with the HF method for theoretical calculations (Tosun and Özmen, 2010: 75-82). It was found that scaled vibrational frequencies are in good agreement with the experimental data. And also the performance of the methods and basis sets, which were used in this study, was investigated. It was found that the DFT-B3LYP method with a 6-311++G(d,p) basis set is the most successful procedure for frequency calculations (Bolukbasi and Akyuz, 2005: 961-971). Similarly, AYŞİN ZÜLFİKAROĞLU in (2016) used different spectroscopic techniques such as NMR, XRD, IR and UV-Vis spectroscopy to study experimentally the optical properties of the Isonitrosoacetophenone and compared the experimental results with that obtained from the DFT methods, she obtained good agreement between theoretical and experimental results (Golzarı and Pishkena, 2019). In this work, by using the gaussian view software, we generate the isonitrosoacetophenone Uv-Vis spectra using HF and DFT methods. The oscillator strength and epsilon, the absorption coefficients and the band-gap energy was calculated and plotted, and the results of the two techniques were compared.

Material and Method

The material used in this work was isonitrosoacetophenone (INAP) C₈H₇NO₂. DFT and HF different basic methods (6-31g, 6-311g and 6-311g (d) in the Gaussian view software were used for simulation of the UV of the INAP material. The material was built by connecting its atoms with an accurate bonding position (single and double). The bond length is adjusted, so that the force strength, absorption coefficients, and the wavelengths exist in the UV part of the electromagnetic spectrum. The results of the UV data were

recorded in each method then the comparison between the DFT and HF and experimental UV spectrometer results were carried out (Fig. 1).

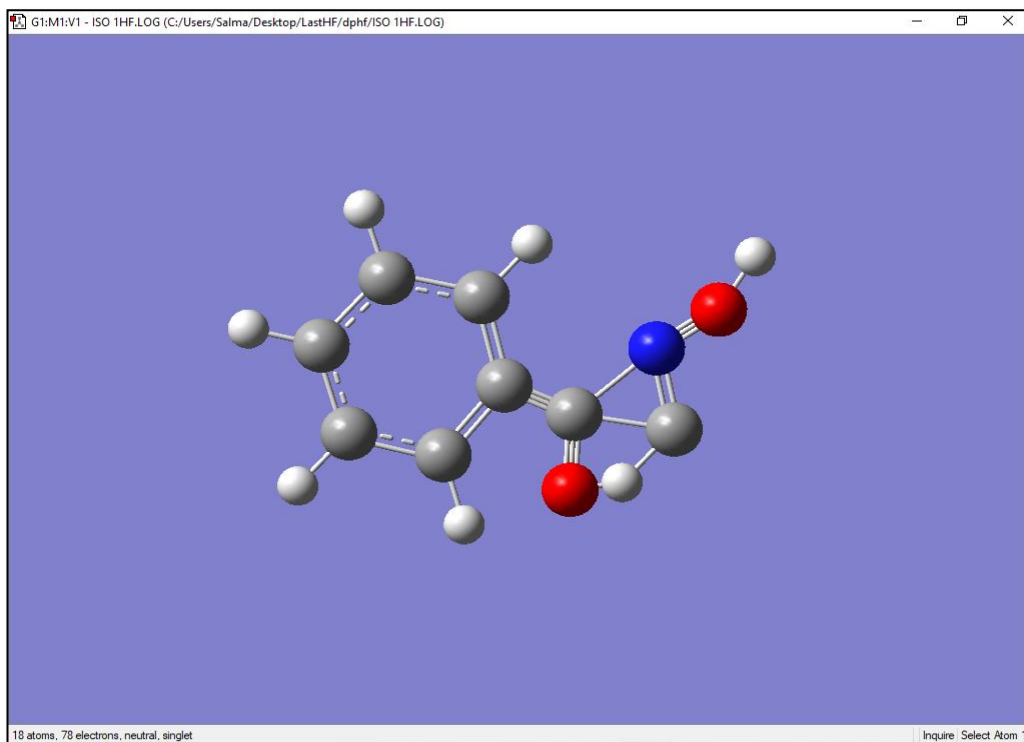


Fig. 1. Gaussian view user interface with highlighted results option shows UV-Vis

Results

Fig. 2 demonstrates the simulation of the UV of the Isonitrosoacetophenone material using Gaussian software DFT (B3LYP basis set 6-311g).

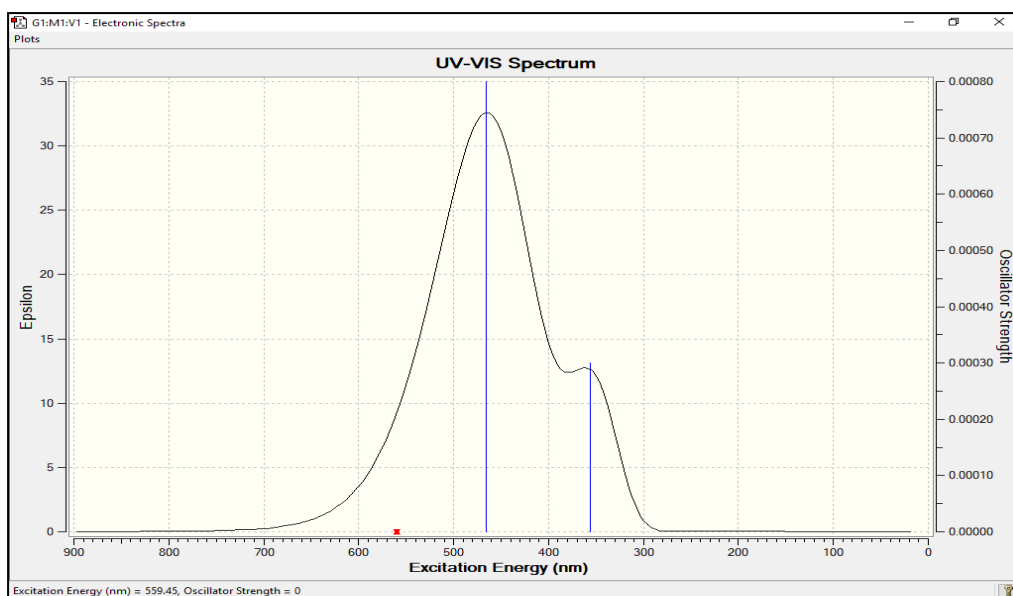


Fig. 2. Simulation of the UV of the Isonitrosoacetophenone material using Gaussian software DFT (B3LYP basis set 6-311g)

Fig. 3 shows simulation of the UV of the Isonitrosoacetophenone material using Gaussian software DFT (B3LYP basis set 6-311g(d)).

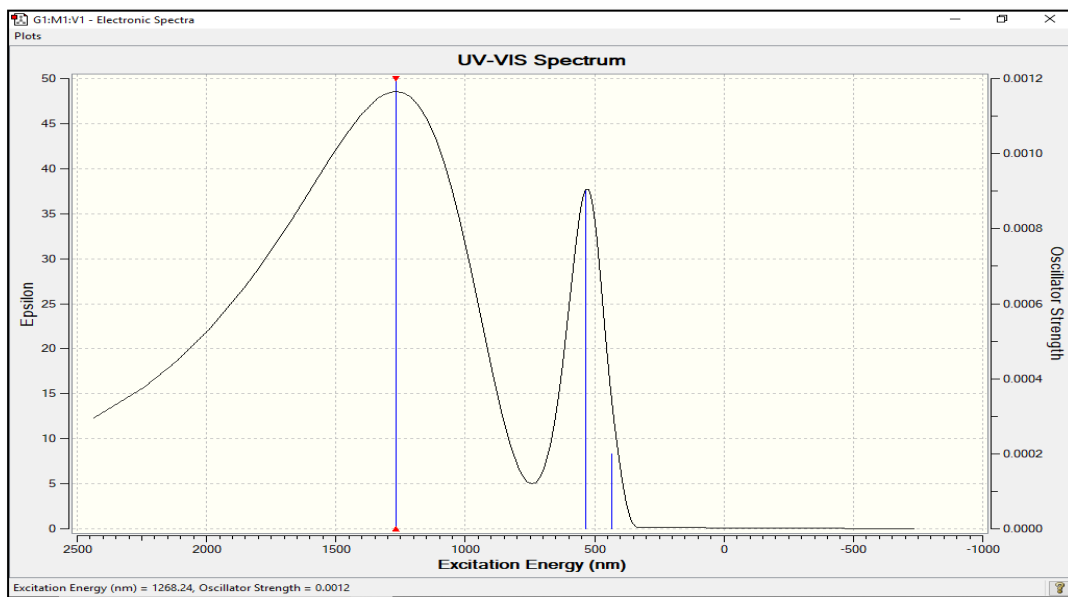


Fig. 3. Simulation of the UV of the Isonitrosoacetophenone material using Gaussian software DFT (B3LYP basis set 6-311g(d))

Fig. 4 demonstrates simulation of the UV of the Isonitrosoacetophenone material using Gaussian software DFT (B3LYP basis set 6-311g (d,p)).

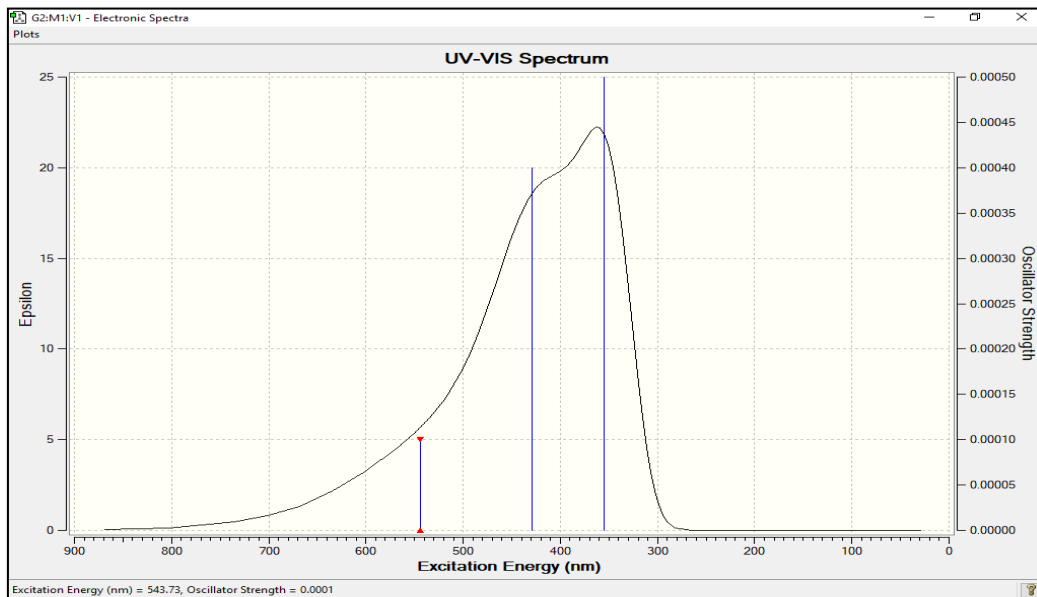


Fig. 4. Simulation of the UV of the Isonitrosoacetophenone material using Gaussian software DFT (B3LYP basis set 6-311g (d,p))

Fig. 5 presents simulation of the UV of the Isonitrosoacetophenone material using Gaussian software HF (basis set 6-311g).

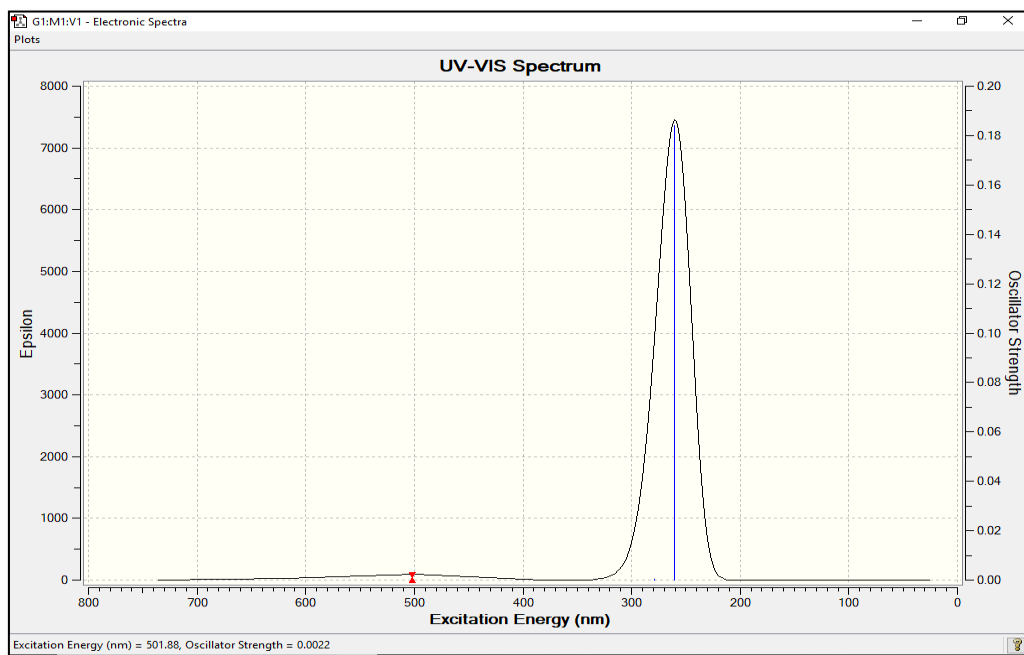


Fig. 5. Simulation of the UV of the Isonitrosoacetophenone material using Gaussian software HF (basis set 6-311g)

Fig. 6 shows simulation of the UV of the Isonitrosoacetophenone material using Gaussian software HF (basis set 6-311g(d))

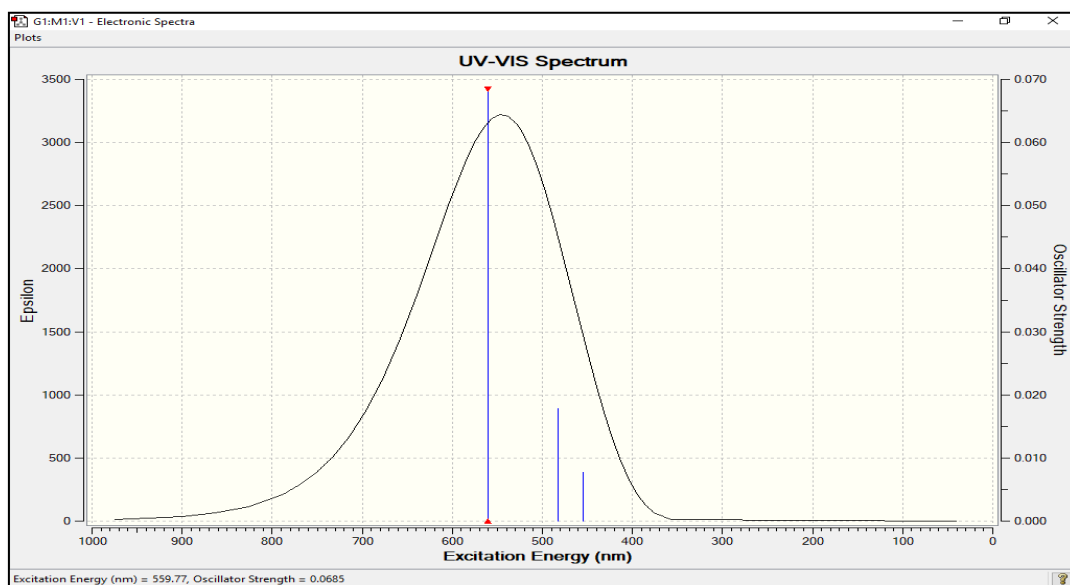


Fig. 6. Simulation of the UV of the Isonitrosoacetophenone material using Gaussian software HF (basis set 6-311g(d))

Fig. 7 refers to simulation of the UV of the Isonitrosoacetophenone material using Gaussian software HF (basis set 6-311g (d,p))

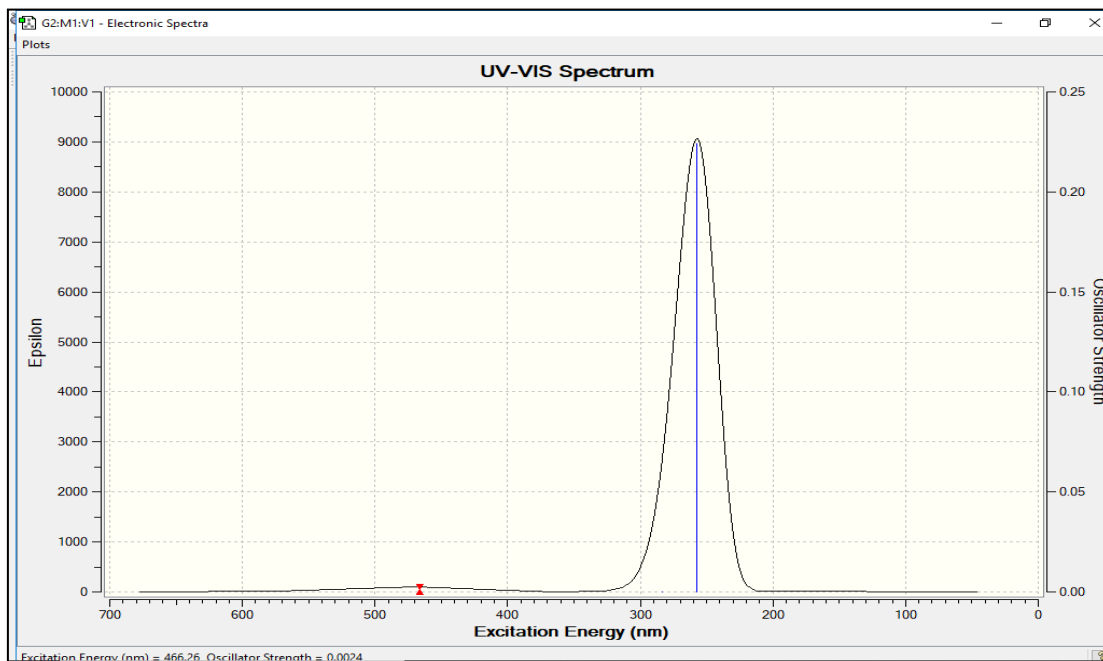


Fig. 7. Simulation of the UV of the Isonitrosoacetophenone material using Gaussian software HF (basis set 6-311g (d,p))

The next Fig. 8 presents the experimental results of the UV of the Isonitrosoacetophenone material

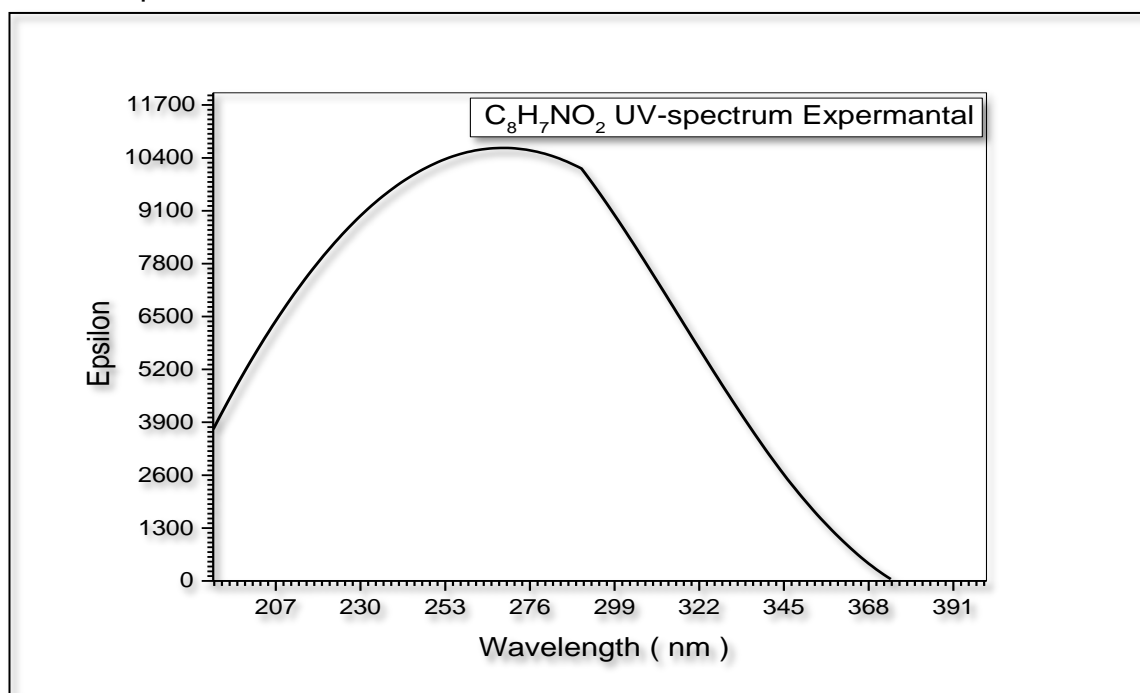


Fig. 8. Experimental results of the UV of the Isonitrosoacetophenone material

Also Table 1 refers to the experimental and theoretical absorption coefficients of (INAP) $C_8H_7NO_2$ and the wavelengths are in the UV part of the electromagnetic spectrum.

Table 1. The experimental and theoretical absorption coefficients of (INAP) $C_8H_7NO_2$ and the wavelengths are in the UV part of the electromagnetic spectrum

Samples	λ (nm)	Absorption Coefficient (Epsilon) (M.cm ⁻¹)
DFT (billy3best sat g 311)	370	14.7
DFT (billy3best sat g 311d)	370	14.7
DFT (billy3best sat g 311dg)	370	22.5
HF (billy3best sat g 311)	270	7500
HF (billy3best sat g 311d)	370	1400
HF (billy3best sat g 311dg)	270	9100
Experimental	270	10676

Discussion

The Fig. 1-7 show the isonitrosoacetophenone molecule built in the Gaussian view software using DFT and HF theoretical methods at different basic methods 6-31g, 6-311g and 6-311g (d). Fig. 8 shows the experimental spectrum, the single and double bonds were shown in their exact position as the chemical formula of the isonitrosoacetophenone molecule. The theoretical electronic excitation energies, the wavelength of the excitation and oscillator strengths were calculated and listed in the Table 1. HF and DFT are able to detect accurate absorption wavelengths at a UV that correspond to vertical electronic directory transitions. Practically, the study of solvent effect on the area of (270 nm) as shown on the experimental results equal [10676 M.cm⁻¹ for experimental, 7500 M.cm⁻¹ for HF (6-311g basis set) and 9100 M.cm⁻¹ for HF (6-311g(d) for vertical excitation energy of electronic spectra. However, the wavelength of (370 nm) shows that, the value of HF (6-311g(d) equal to 1400 M.cm⁻¹, equal 14.7 M.cm⁻¹ for (DFT (B3LYP basis set 6-311g) and DFT (B3LYP basis set 6-311 (d) basis set and equal 22,5 M.cm⁻¹ for DFT (B3LYP best sat 6-311g(d).

Conclusion

The theoretical UV-Visible spectrum absorption for isonitrosoacetophenone (INAP) $C_8H_7NO_2$ was recorded. The HFT and HF absorption shifts were calculated by B3LYP function with different basic methods. In this article, the UV-Vis results were generated from the simulation using the Gaussian software were compared with UV-Vis spectrometer.

References

- Alama, M., Alam, M.J., Azaz, Sh., Parveen, M., Park, S., Ahmad, Sh. (2018). DFT/TD-DFT calculations, spectroscopic characterizations (FTIR, NMR, UV-vis), molecular docking and enzyme inhibition study of 7-benzoyloxy coumarin. *Computational Biology and Chemistry*, 73, 65-78. <https://doi.org/10.1016/j.compbiolchem.2018.01.007>
- Basden, K.A., Tye, J.W. (2014). Introduction to Density Functional Theory: Calculations by Hand on the Helium Atom. *J. Chem. Educ.*, 91(12), 2116-2123. <https://doi.org/10.1021/ed5004788>
- Bolukbasi, O., Akyuz, S. (2005). Computational Vibrational Study on Coordinated Nicotinamide, *J. Mol. Struct.*, 744-747, 961-971. Available at: https://www.academia.edu/24844535/Computational_vibrational_study_on_coordinated_nicotinamide
- Erdogdu, Y., Sertbakan, T.R., Dereli, O., Gulluoglu, M.T., Yurdakul, S. (2017). Experimental and Theoretical Vibrational Spectroscopic Study of Zinc (II) Halide

Complexes of 4-Acetylpyridine Laboratoire. GU J Sci, 30(4), 553-563. Available at: <https://dergipark.org.tr/tr/download/article-file/380207>

Friesner, R.A. (2005). Ab initio quantum chemistry: Methodology and application. Richard A. Friesner PNAS, 102 (19), 6648-6653. <https://doi.org/10.1073/pnas.0408036102>

Frisch, Æ.H., Hratchian, H.P., Dennington II, R.D., Keith, T.A., Millam, J. (2009). GaussView 5 Reference. Wallingford: Gaussian, Inc. Available at: <https://wiki.crc.nd.edu/w/images/d/d7/Gaussview-5-ref.pdf>

Golzari, A., Pishkena, H.N. (2019). Vibrational Analysis of Fullerene Hydrides Using AIREBO Potential. Scientia Iranica: International Journal of Science and Technology. <https://doi.org/10.24200/SCI.2019.51307.2105>

Kaczmarek, H., Królikowski, B., Klimiec, E., Chylińska, M., Bajer, D. (2019). Advances in the study of piezoelectric polymers. Russian Chemical Reviews, 88(7), 749-774. Available at: <http://mi.mathnet.ru/rcr4259>

Kaya, Yu., Yilmaz, V.T., Buyukgungor, O. (2016). Synthesis, Spectroscopic, Structural and Quantum Chemical Studies of a New Imine Oxime and Its Palladium(II) Complex: Hydrolysis Mechanism. Molecules, 21(1), 52. <https://doi.org/10.3390/molecules21010052>

Lamsabhi, A.M., Yáñez, M., Móa, O., Trujillo, C., Blancob, F., Alkorta, I., Elguero, J., Caballeroc, E., Rodríguez-Morgadec, M.S., Claessensc, Ch.G., Torres, T. (2011). TDDFT study of the UV-vis spectra of subporphyrazines and subphthalocyanines, Journal of Porphyrins and Phthalocyanines J. Porphyrins Phthalocyanines, 15(11), 1220-1230. <https://doi.org/10.1142/S1088424611004154>

Özmen, A., Tapramaz, R., Koksall, F., Yuksel, H. (2000). İzonitrosoasetofenon ve Fenilgliksim Tek Kristallerinde Tuzaklanmış İminoksi Radikallerinin Elektron Spin Rezonansı. Selçuk Üniversitesi Fen Fakültesi Fen Dergisi, 1 (16), 67-79. Available at: <https://dergipark.org.tr/tr/pub/sufefd/issue/23172/247518>

Raut, R.D., Jadhav, S.Z., Bagade, P.N., Nandeshwar, S.T. (2011). Synthesis and physico-chemical studies of Cu(II), Ni(II), Co(II) complexes with p-chloroisnitroso acetophenone (P-CIINAP). J. Chem. Pharm. Res., 3(6), 195-199. Available at: <http://www.jocpr.com/articles/synthesis-and-physico-chemical-studies-of-cuii-niii-coii-complexes-with-pchloroisnitroso-acetophenone-pclinap.pdf>

Seshadri, S., Rasheed, M.P. (2016). Molecular structure, vibrational, UV, NMR, molecular electrostatic surface potential and HOMO-LUMO Analysis of 1,4-dichloro-2-nitrobenzene. Research Invention: International Journal of Engineering and Science, 6(4), 6-18. Available at: <http://www.researchinvention.com/papers/v6i4/B060406018.pdf>

Sing, Ya. (2005). The oxime bond formation as a useful tool for the preparation of oligonucleotide conjugates. Comptes Rendus Chimie, 8(5), 789-796. <https://doi.org/10.1016/j.crci.2005.02.007>

Tosun, Z. (2010). Fenilgliksim Molekülünün Titresimlerinin Analizi. KONYA, 36, 65-74. Available at: <https://dergipark.org.tr/tr/download/article-file/215355>

Tosun, Z., Özmen, A. (2010). İzonitrosoasetofenon Molekülünün Titresimlerinin Analizi. KONYA, 36, 75-82 Available at: <http://fendergisi.selcuk.edu.tr/fen/article/view/3/2>