

REPUBLIC OF TURKEY
FIRAT UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES



**ELECTRON DENSITY CALCULATIONS
OF COMPLEX MOLECULES**

Hamd Kareem MAHMOOD

MASTER THESIS

Department: Physics

Program: Atom and Molecular Physic

April 2017

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Hamd Kareem MAHMOOD

TURKEY – Elazig - 2017

SUMMARY

FTIR spectroscopy is related to the vibration modes of a molecule. To calculate the vibrational modes, electron density functions and molecular orbitals density function theory (DFT) method was applied. In this thesis, we have calculated infrared spectroscopy, electron densities and molecular orbital for many different big molecules by implementing DFT method. All the results are interpreted in detail.



ÖZET

KOMPLEKS MOLEKÜLLERİN ELEKTRON YOĞUNLUĞUNUN HESAPLANMASI

Bu tez çalışmasında bazı molekülerin electron yoğunlukları DFT metodu ile hesaplandı. Ayrıca aynı sistemlerin moleküler orbitalleri ve FTIR spektrumları da DFT metodu ile hesaplandı. Bütün sonuçlar detaylı olarak yorumlandı.

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ABBREVIATIONS

VIS	: Visible
UV	: Ultraviolet
IR	: Infrared
FTIR	: Fourier Transform Infrared
DFT	: Density Functional Theory
HOMO	: Highest Occupied Molecular Orbital
LUMO	: Lowest Unoccupied Molecular Orbital
ΔE	: Energy Band Gap



1. INTRODUCTION

Fourier Transform Infrared spectroscopy is one of the best analytical techniques, which exists for today's researchers. The benefits of infrared spectroscopy are that practically any case in approximately any state might be studied [1, 2].

Fourier Transform Infrared spectrometers have been monetarily accessible since 1940s. The best noteworthy advances in infrared spectroscopy, notwithstanding, have come to fruition due to the presentation of Fourier-change spectrometers. [1, 3].

The essential thoughts in infrared spectroscopy is related to definitions of the vibrations of molecules will be taken here, crucial to the explanation of infrared spectra [1, 3]. The energy of infrared light is no longer adequate to actuate moves of valence electrons. Rather, infrared radiation energizes vibrational and rotational movements in molecules. As for the changes in the energy transmission from the radioactivity to the molecule, the principles of IR spectroscopy are similar as those of VIS/UV spectroscopy or other spectroscopic systems. The absorption of infrared light is again considered by the Bouger-Lambert-Beer Law.

Infrared spectra are usually introduced by a plot of the rate of transmission versus the wavenumber in cm^{-1} (rather than a plot of absorbance versus the wavelength of nm in VIS spectroscopy). An average IR range is along these lines recorded from around 4 000 to 10 000 cm^{-1} (furthest utmost) to around 100-800 cm^{-1} (lower limit) [1, 5].

Many techniques such as Fourier Transform Infrared (FTIR) spectroscopy is a common spectroscopic technique which can be widely used in inorganic and organic chemistry. One of the main goals of FTIR is analysis to determine the chemical functional groups in the samples [4].

2. SPECTROSCOPY

Spectroscopy is the study of the interaction of energy and matter. The interest of the energy of diverse magnitudes causes diverse changes in substance. The magnitude of energy absorbed is determined by the structure of the substance below study.

Assurance of the entire atomic structure of an obscure substance is made less demanding when we have more pieces of information. More complex formulae can prompt to handfuls or even several conceivable outcomes.

A technique that accomplishes this objective is infrared (IR) spectroscopy. In this procedure, we uncover the atom being referred to infrared photons. As we will learn in the following few areas, functional groups absorb infrared photons of typical energies. We then make a plot of photon energy versus intensity of absorption, called the infrared range. Along these lines, IR spectroscopy permits us to reason the functional groups that are available and missing in a molecule [6,7].

An infrared spectrum as can be seen in Figure 2.1 contains a plot of extending frequency in cm^{-1} versus intensity as measured by % transmittance.

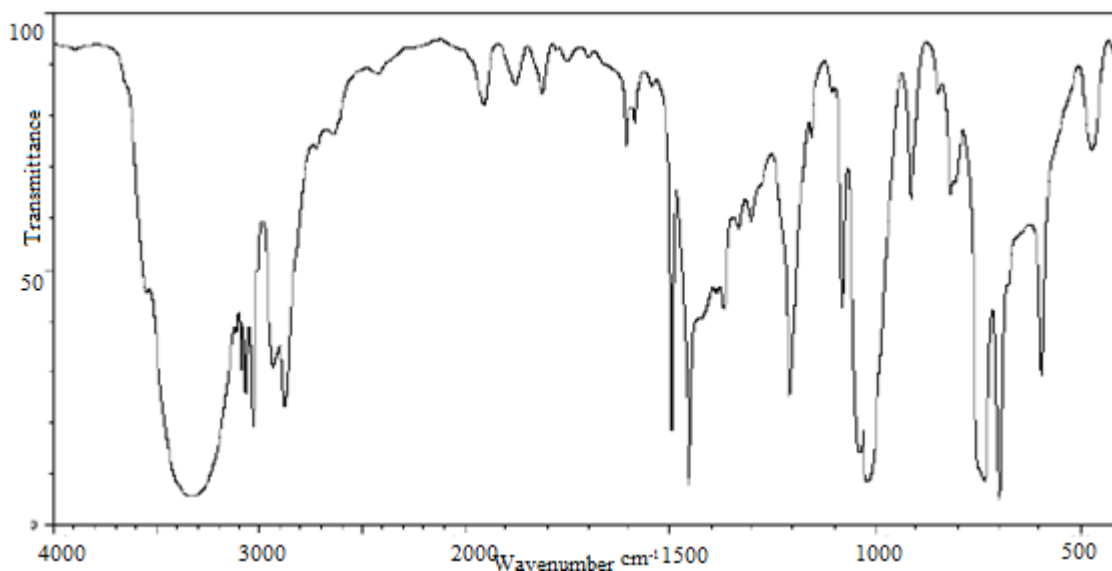


Figure 2.1. This IR range of benzyl alcohol is a plot of photon energy using the related wavenumber scale versus intensity as measured by % transmittance [8].

Spectroscopy was initially the investigation of the communication amongst radiation and matter as an element of wavelength (λ). As it can be seen from Figure 2.2 the dispersion of lights is travel through a triangular prism and it comes out with a different wavelength.

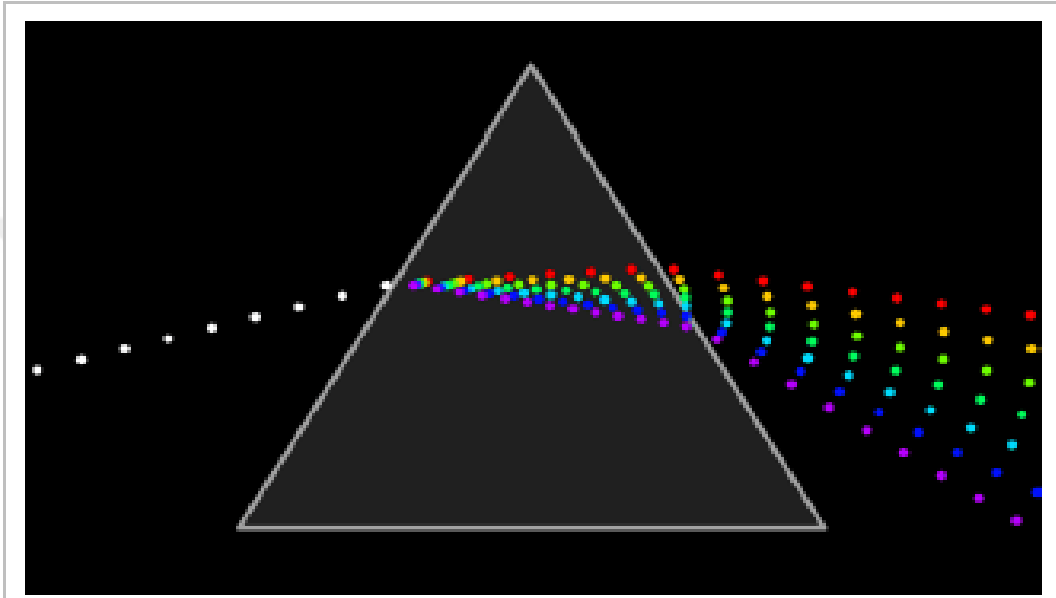


Figure 2.2. Dispersion of light as it travels through a triangular prism [7].

Spectroscopy is single most vital devices in a researcher's toolbox. Space experts utilize spectroscopy to study light from various objections in the Universe. Light is energy and can be considered as either waves or particles [8].

Spectrometry is the spectroscopic technique used to assess the concentration or amount of a given species. Spectroscopy or spectrometry is also heavily used in astronomy and remote sensing.

2.1. Infrared Radiation

Infrared radiation is a kind of electromagnetic radiation with a wavelength from 0.74 μm to visible light (100 μm) and was found by British space expert William Herschel. IR

radiation was found by British space expert William Herschel in his teaching of the Sun in 1800. In any case, he was not ready to translate it accurately and this discovery was overlooked. More than a half-century go before J. C. Maxwell reasoned the equations which involve the basic laws of electromagnetism (1864) [9,11].

Toward the start of the 20. century, A.A Glagoleva Arkadieva got the radio waves with a wavelength equivalent to 80 μm . In this way, it was tentatively demonstrated that there exists a continuous transition from the IR radiation to radio waves [9-11].

2.2. Infrared Spectroscopy

FTIR spectroscopy is utilized to learning the vibrational motions of atoms [12] and is recognizing how certain atoms are attached to each other or how they are gathered in a molecule.

There are two kinds of vibrations motions that cause an absorption in an IR range of frequency. Stretching includes a displacement along the bond axis. Bending includes an alteration in the bond angle between two bonds and an atom mutual to both. These two motions are displayed in Figure 2.3.

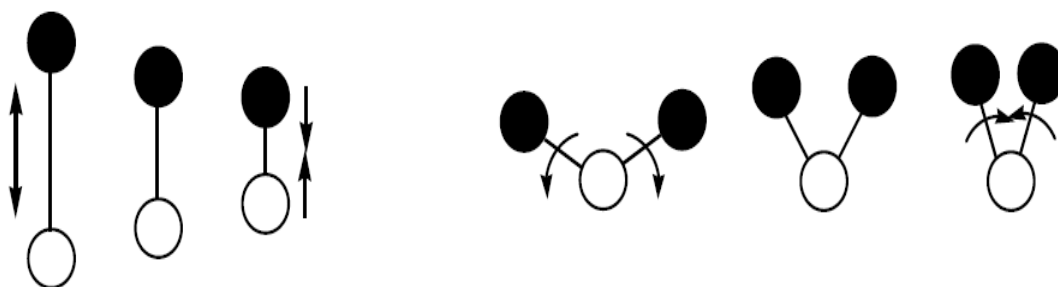


Figure 2.3. Stretching and Bending Vibrations of a diatomic molecule [12].

For example, in Figure 2.4 the borohydride anion (BH_4) example is shown and it has two vibrational modes that can be detected by IR spectroscopy.

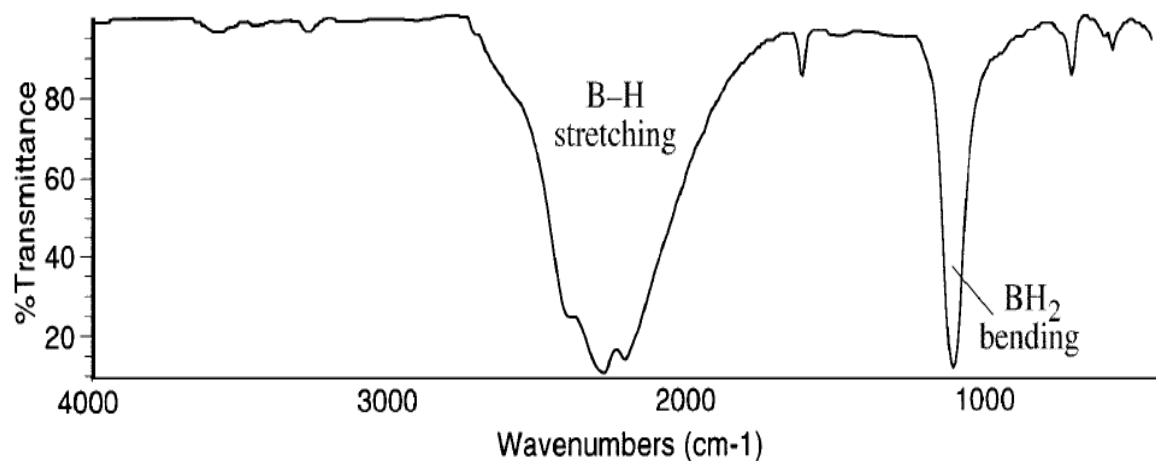


Figure 2.4 Infrared spectrum of NaBH_4 (KBr pellet) [12].

Another example is CO_2 molecule which is displayed in Figure 2.5 and can produce an IR spectrum since the two $\text{C}=\text{O}$ bonds can stretch in an asymmetric mode and furthermore twist to deliver changes in the dipole moment [12-14].

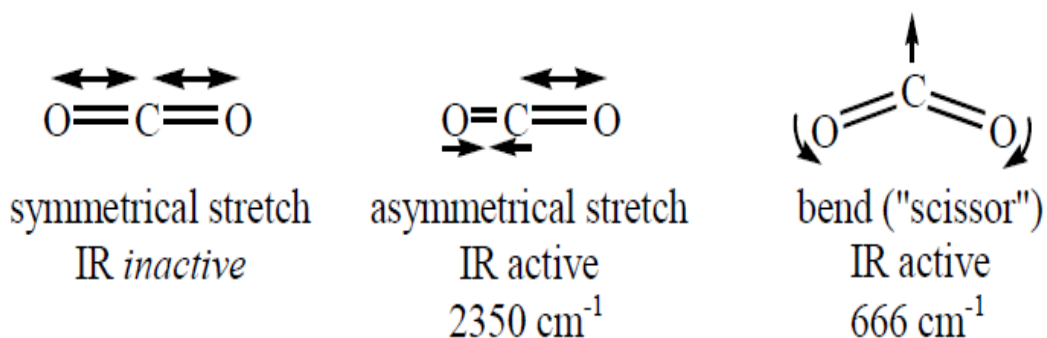


Figure 2.5. Stretching and Bending Vibrations in CO_2 molecule [12].

More complex molecules have many bonds. For instance, the atoms in a CH_2 (C_2H_4) which is a molecule that studied for this thesis, generally found in organic compounds can vibrate in six diverse ways: symmetrical and anti-symmetrical stretching, scissoring, rocking, wagging and twisting as can be seen in Figure 2.6 [15].

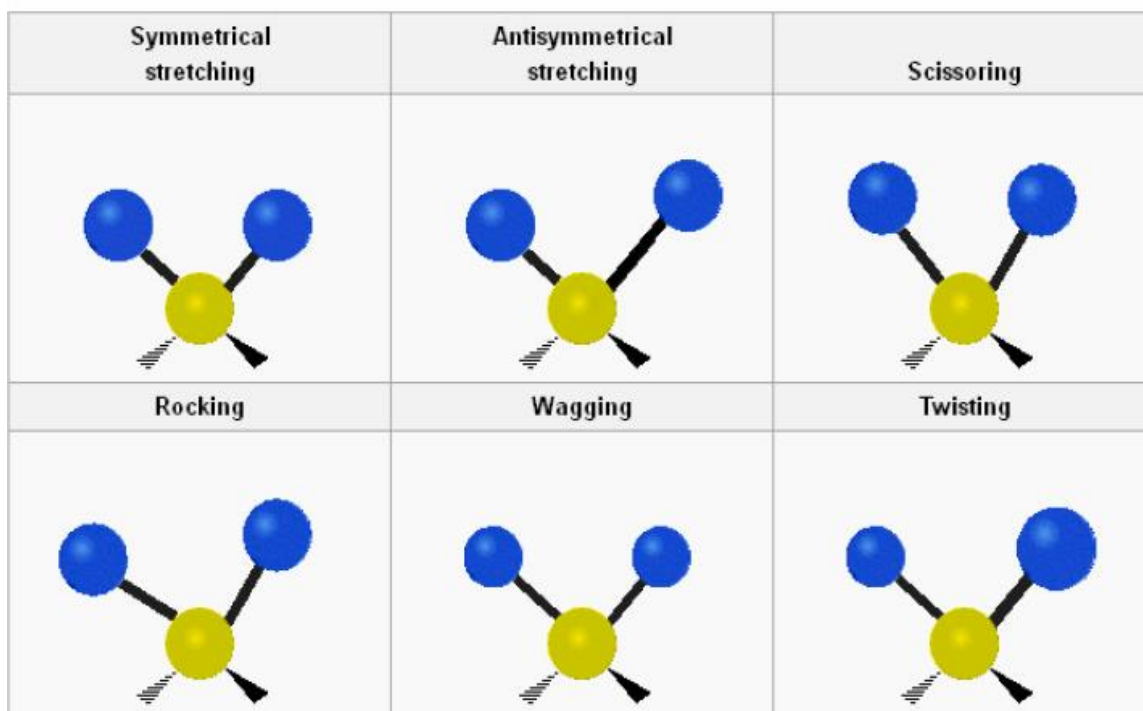
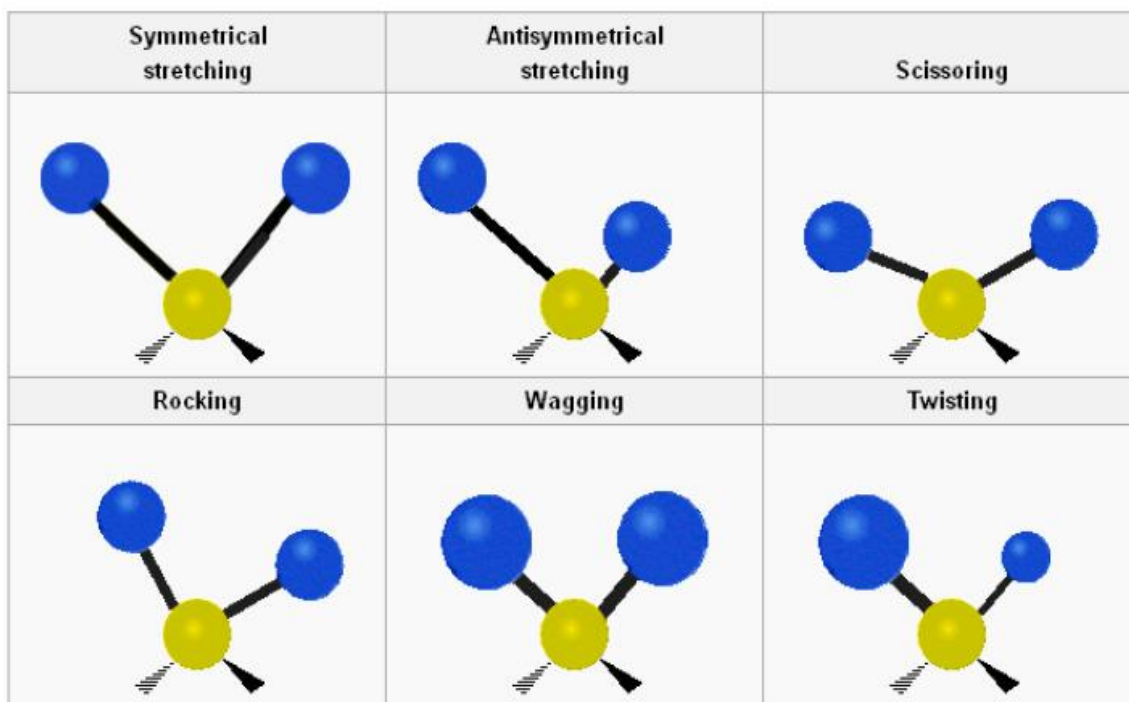


Figure 2.6. Types of Vibration modes [15].

3. THEORY OF FTIR ABSORPTION SPECTROSCOPY

Someone can excite a molecule via two physical mechanisms. One of them is the absorption of light and the other is scattering a photon. Figure 3.1 has demonstrated direct absorption mechanism. The energy contrast $h\nu_k$ between two vibrational energy levels, the ground and the final vibrational state can be given [16]

$$h\nu_k = h\nu_f - h\nu_i \quad (3.1)$$

The energy difference between two spectral lines can be given as

$$h\nu_0 - h\nu_R = h\nu_f - h\nu_i \quad (3.2)$$

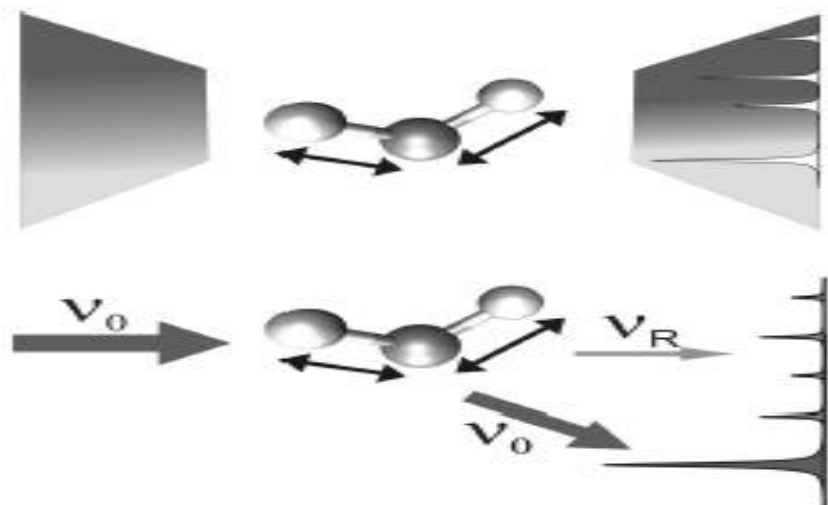


Figure 3.1. Outline of the excitation of molecular vibrations in IR (top) and Raman (bottom) spectroscopy [16].

Vibrational transitions might be related to a rotational transition that must be resolved in high-determination spectra of molecules in the gas stage. Along these lines, vibration-rotation spectra will not be related to this thesis [15,16].

3.1 Molecular Vibrations

The two masses with m_A and m_B , on movement of the spheres along the x-axis from the local position by Δx , a reinstating force F_x follows up on the spheres, which as per Hooke's law, is given by [17].

$$F_x = -f\Delta x \quad (3.3)$$

where f is force constant. The potential energy V then hinge on the square of the dislodging from the symmetry position

$$V = \frac{1}{2}f\Delta x^2 \quad (3.4)$$

From the kinetic energy, one gets

$$T = \frac{1}{2}\mu(\Delta \dot{x})^2 \quad (3.5)$$

Where μ is, the reduced mass and can be defined by

$$\mu = \frac{m_A \cdot m_B}{m_A + m_B} \quad (3.6)$$

Because of the conservation of energy, one can get

$$0 = \frac{dT}{dt} + \frac{dV}{dt} = \frac{1}{2} \frac{d(\Delta \dot{x}^2)}{dt} + \frac{1}{2} f \frac{d(\Delta x^2)}{dt} \quad (3.7)$$

and with the Newton equation of motion

$$\frac{d^2 \Delta x}{dt^2} + \frac{f}{\mu} \Delta x = 0 \quad (3.8)$$

Equation (3.8) characterizes the differential equation for a harmonic motion and given as

$$\Delta x = A \cdot \cos(\omega t + \varphi) \quad (3.9)$$

here A, ω , and φ are the amplitude, circular frequency, and phase, respectively.

Joining Eq. (3.9) with second derivative one can get

$$\frac{d^2 \Delta x}{dt^2} + \omega^2 \Delta x = 0 \quad (3.10)$$

And we can obtain the frequency,

$$\omega = \sqrt{\frac{f}{\mu}} \quad (3.11)$$

The frequency in wavenumbers as in cm^{-1} [16-19].

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f}{\mu}} \quad (3.12)$$

4. DENSITY-FUNCTIONAL THEORY

DFT is a variationally technique that is currently the greatest effective approach for computing the electronic structure of matter. Its applicability ranges from molecules, atoms, and solids to nuclei and quantum. The DFT is derived from the N-particle Schrödinger equation and is completely communicated as far as the density spreading of the ground state and the single particle wave function [20-22].

4.1. Equations in Density Functional Theory

Density functional theory is a standout amongst the most popular and successful quantum mechanical ways to deal with matter.

In quantum mechanics, we discover that all data we can have in a given framework is contained in the framework's wave function, Ψ which for a single electron transition in a potential $v(r)$ can be given [21,23,24].

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + v(r) \right] \Psi(r) = \epsilon \Psi(r). \quad (4.1)$$

If here is more than one electron the Schrödinger's equation

$$\left[\sum_i^N \left(-\frac{\hbar^2 \nabla_i^2}{2m} + v(r_i) \right) + \sum_{i<j} U(r_i, r_j) \right] \Psi(r_1, r_2, \dots, r_N) = E \Psi(r_1, r_2, \dots, r_N), \quad (4.2)$$

here N is the quantity of electrons and $U(r_i, r_j)$ is the electron-electron interaction. For a Coulomb framework, one can write

$$\hat{U} = \sum_{i<j} U(r_i, r_j) = \sum_{i<j} \frac{q^2}{|r_i - r_j|}. \quad (4.3)$$

the Coulomb interaction, similarly as the kinetic energy operator

$$\hat{T} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 \quad (4.4)$$

is the similar for any nonrelativistic framework. For an atom

$$\hat{V} = \sum_i v(r_i) = \sum_i \frac{Qq}{|r_i - R|}, \quad (4.5)$$

Where R the nuclear position and Q is the nuclear charge. For a molecule or a solid the potential can be written as

$$\hat{V} = \sum_i v(r_i) = \sum_{ik} \frac{Q_k q}{|r_i - R_k|}, \quad (4.6)$$

where the entirety on k reaches out over all nuclei in the structure, each with charge $Q_k = Z_k e$ and position \mathbf{R}_k . The typical quantum-mechanical way to deal with Schrödinger's equation can be abridged by the below sequence equation

$$v(r) \xrightarrow{SE} \Psi(r_1, r_2, \dots, r_N) \xrightarrow{\langle \Psi | \dots | \Psi \rangle} \text{observables}, \quad (4.7)$$

One among the observables that designed in this method is the particle density [21].

$$n(r) = N \int d^3 r_2 \int d^3 r_3 \dots \int d^3 r_N \Psi^*(r, r_2, \dots, r_N) \Psi(r, r_2, \dots, r_N). \quad (4.8)$$

Numerous capable way for explaining Schrödinger's equation have been produced amid many years of battling with the many-body problem [21,25,26].

5. ELECTRON DENSITY

Electron density is the measure of the probability of an electron being available at a particular area. In molecules, areas of electron density are typically found around the atom and around its bonds [27-29].

In quantum, chemical calculations, the electron density $\rho(\mathbf{r})$, is an element of the directions \mathbf{r} , characterized as $\rho(\mathbf{r})d\mathbf{r}$ is the quantity of electrons in a little volume $d\mathbf{r}$. The $\rho(\mathbf{r})$ can be composed of terms as a sum of results of premise functions, ϕ :

$$\rho(\mathbf{r}) = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \phi_{\mu}(\mathbf{r})\phi_{\nu}(\mathbf{r}) \quad (5.1)$$

where P is the density matrix.

Mulliken population examination depends on electron densities in particles and is a method for separating the density between atoms to give a gauge of atomic charges.

6. RESULTS AND DISCUSSION

The theory given above was applied to a different molecular system which is important in theoretical chemistry. For these molecular systems at the beginning of the calculations, two structures are optimized by using DFT method with a simple basis set. After optimized the quantum mechanical calculations were done for the same optimized structure.

6.1. Naphthalene

Figure 6.1 displays the symbolic optimized structure of naphthalene molecule. As it can be seen from the figure the structure is periodic and for this geometry, we implement DFT method with a 6-311G basis set to calculate quantum results. With DFT method, we have calculated vibration modes of the title molecules which give us the infrared information about the molecular systems.

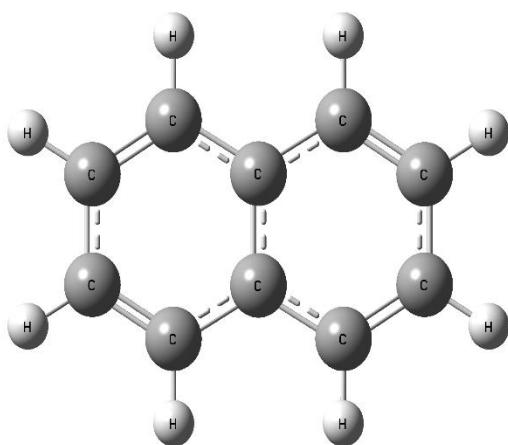


Figure 6.1. Atomic symbolic structure of naphthalene.

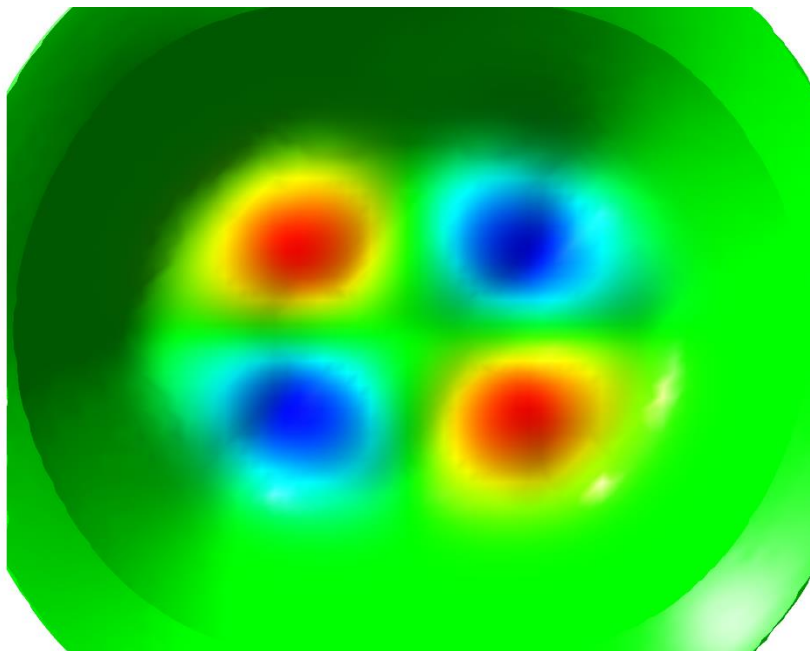


Figure 6.2. electron density of naphthalene.

Figure 6.2 demonstrates the electron density for naphthalene molecule systems. As it can be seen from the figure the density of electron is big around the carbon atoms than hydrogen atoms. These results are obtained with the DFT method by implementing Mulliken population analysis. Figure 6. 3 is showing the molecular orbital for naphthalene molecule. With this figure, one can see very easily the electron density or electron clouds around the molecular systems. For naphthalene, the HOMO energy value is -0.21723 eV and the LUMO energy is -0.03539 eV. The difference between this two values is 0.18184 eV which is an energy band gap for naphthalene molecule. This value is important for the electron transfer from one level to another. An electron which has an energy equal to the bandgap can jump from lower to higher energy level [30-32].

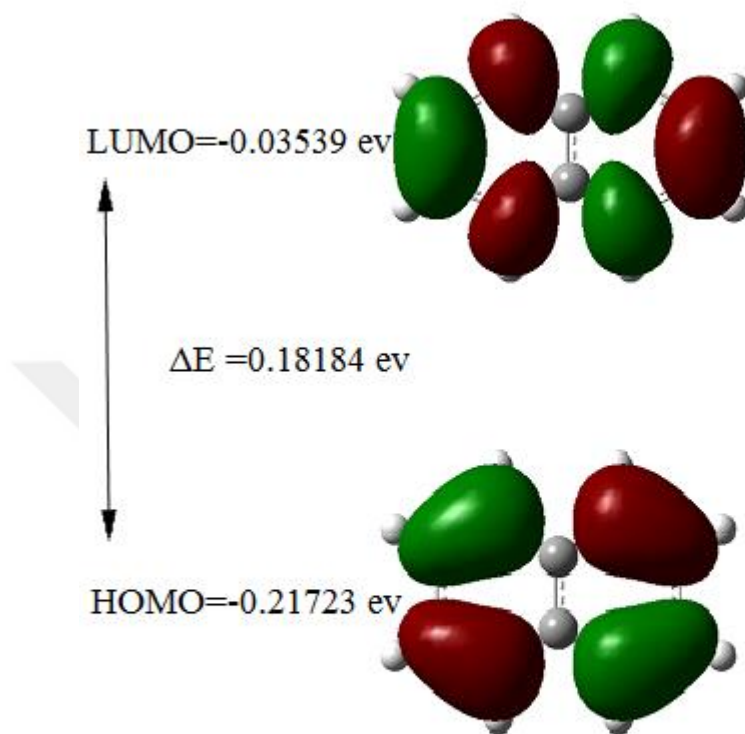


Figure 6.3. HOMO and LUMO energies of naphthalene molecule.

Figure 6.4 is the FTIR spectrum of the naphthalene molecule that has been studied in this thesis. This figure is obtained from the frequency calculations of DFT method. As can be seen from the figure there have been some picks. These picks correspond to the vibration modes of the studied molecules.

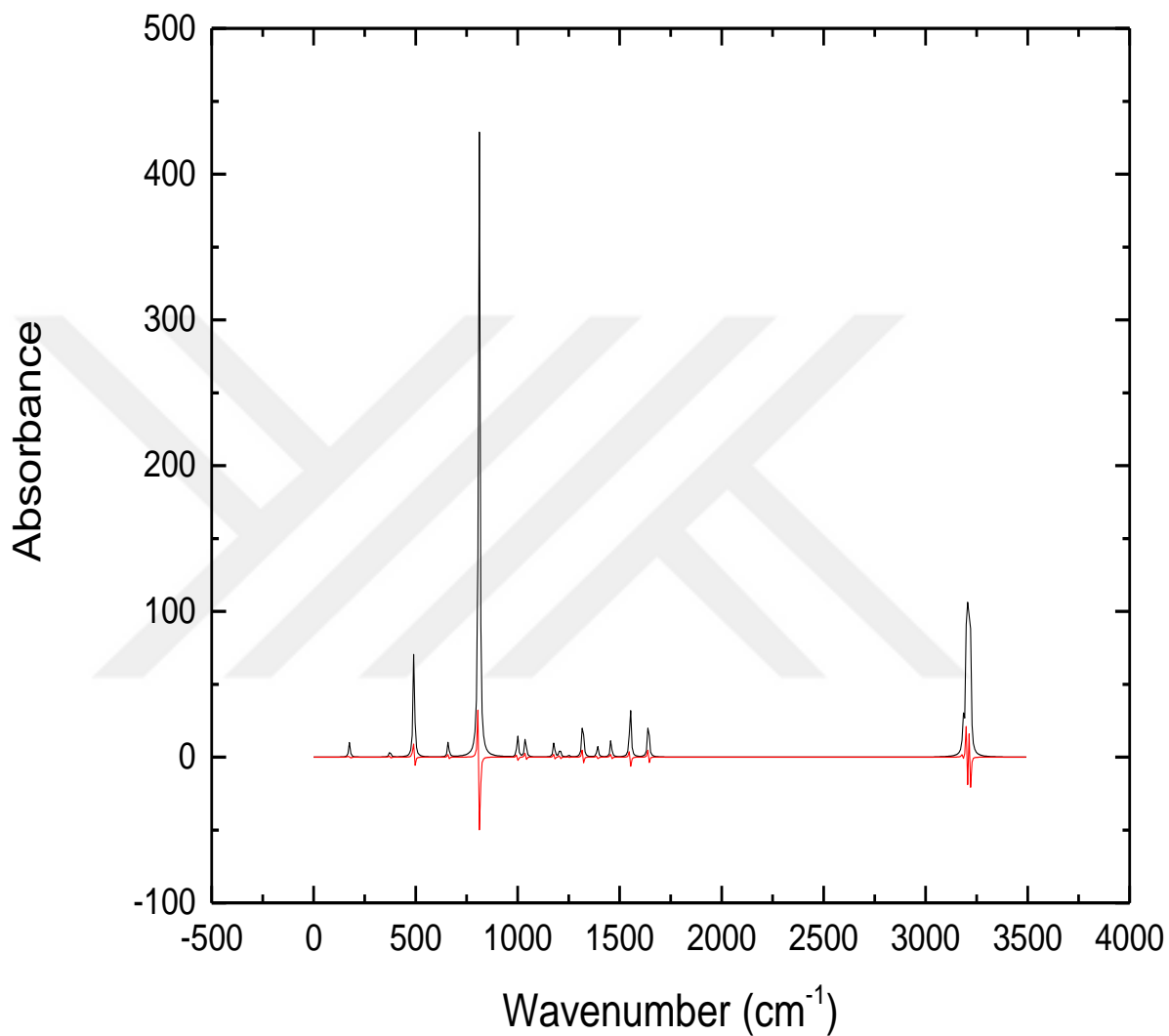


Figure 6. 4. FTIR spectroscopy results for naphthalene.

6.2. Ethene Molecule

Figure 6.5 displays the symbolic optimized structure of ethene molecule. For this molecule, we implement DFT method with a 6-311G basis set to calculate quantum results. With DFT method, we have calculated vibration modes of the title molecules which give us the infrared information about the molecular systems.

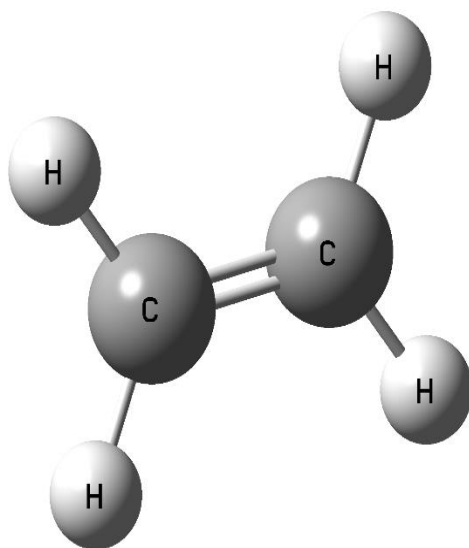


Figure 6. 5. Atomic symbolic structure for the C_2H_4 (Ethene) molecule.

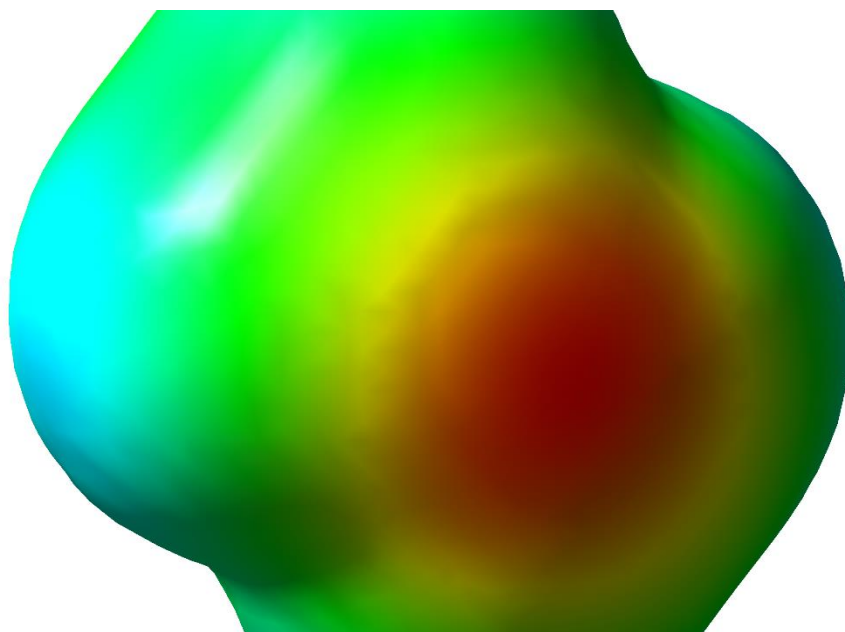


Figure 6. 6. Electron density of the C_2H_4 .

Figure 6.6 demonstrates the electron density for ethene molecule systems. As can be seen from the figure the density of electron is big around the carbon atoms than hydrogen atoms. These results are obtained with the DFT method by implementing Mulliken population analysis.

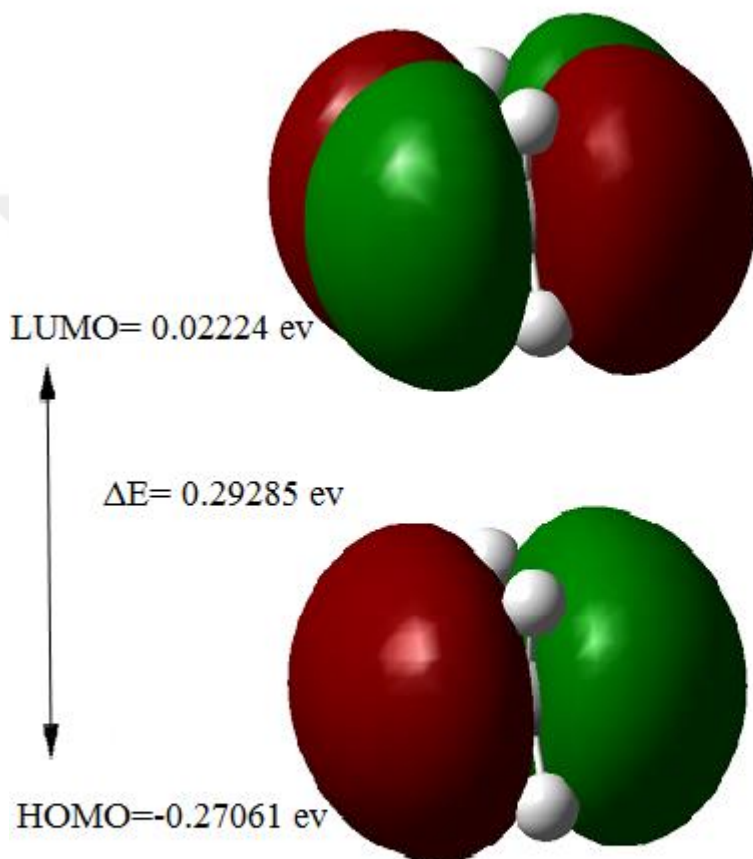


Figure 6. 7. HOMO and LUMO energies of the C_2H_4 molecule.

The HOMO and LUMO values for the C_2H_4 molecule are -0.27061 eV and 0.02224 eV respectively. The energy band gap between HOMO and LUMO is 0.29285 eV as shown Figure 6.7.

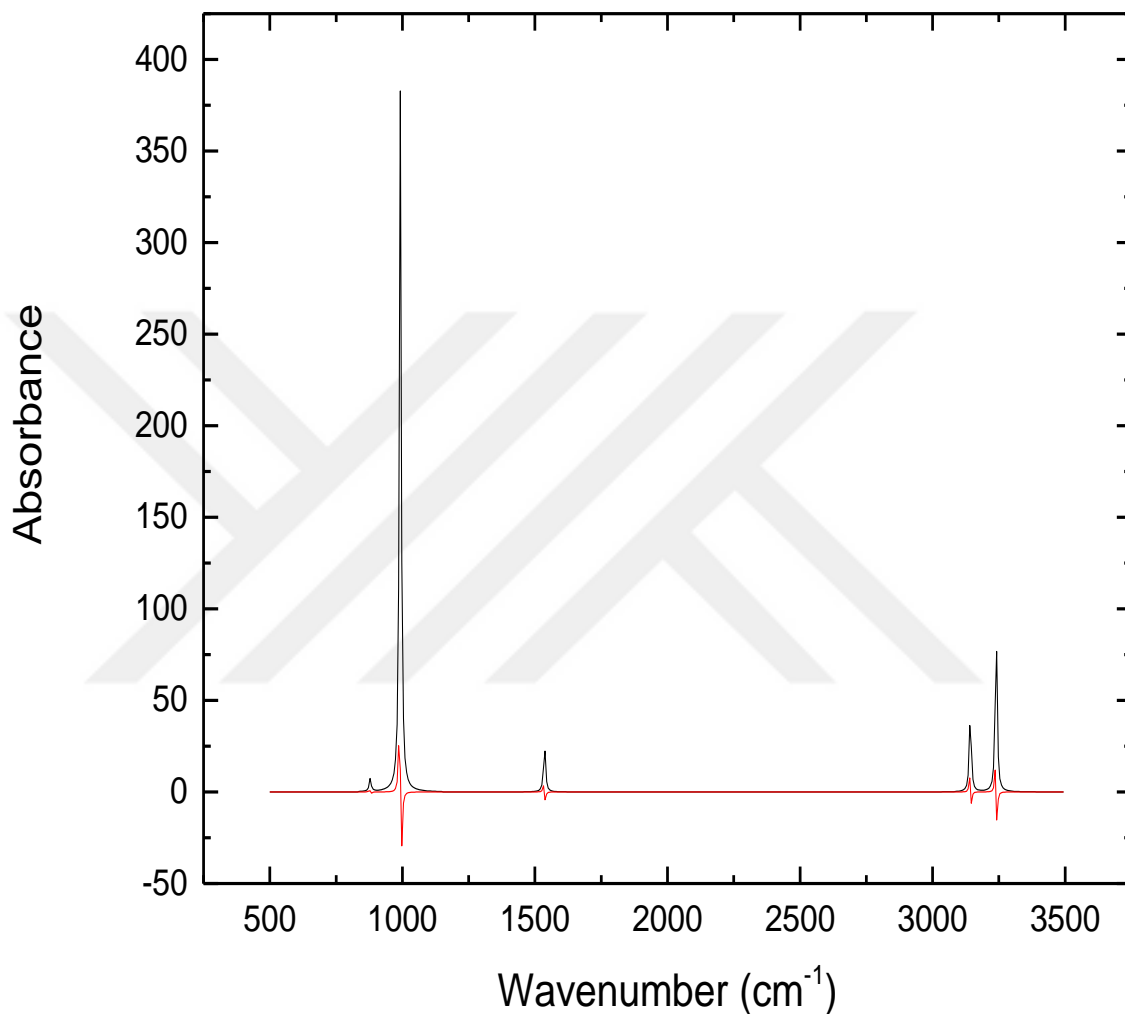


Figure 6. 8. FTIR spectroscopy results for the C₂H₄.

Figure 6.8 is depicted infrared spectroscopy for ethene (C₂H₄). As it can be seen, the naphthalene has more vibration modes than the C₂H₄ molecule and that is why the number of the pick for naphthalene are more than the C₂H₄ molecule.

6.3. Ethyne Molecule

Figure 6.9 displays the symbolic optimized structure of ethyne molecule. For this molecule, we implement DFT method with a 6-311G basis set to calculate quantum results. With DFT method, we have calculated vibration modes of the title molecules which give us the infrared information about the molecular systems.

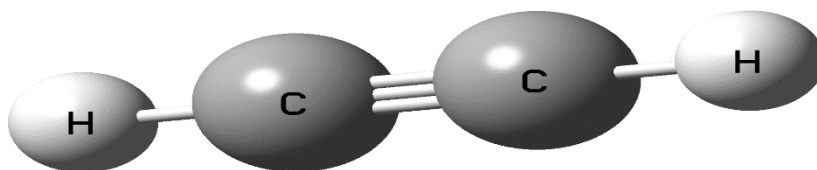


Figure 6. 9. Atomic symbolic structure for the C₂H₂ (Ethyne) molecule.

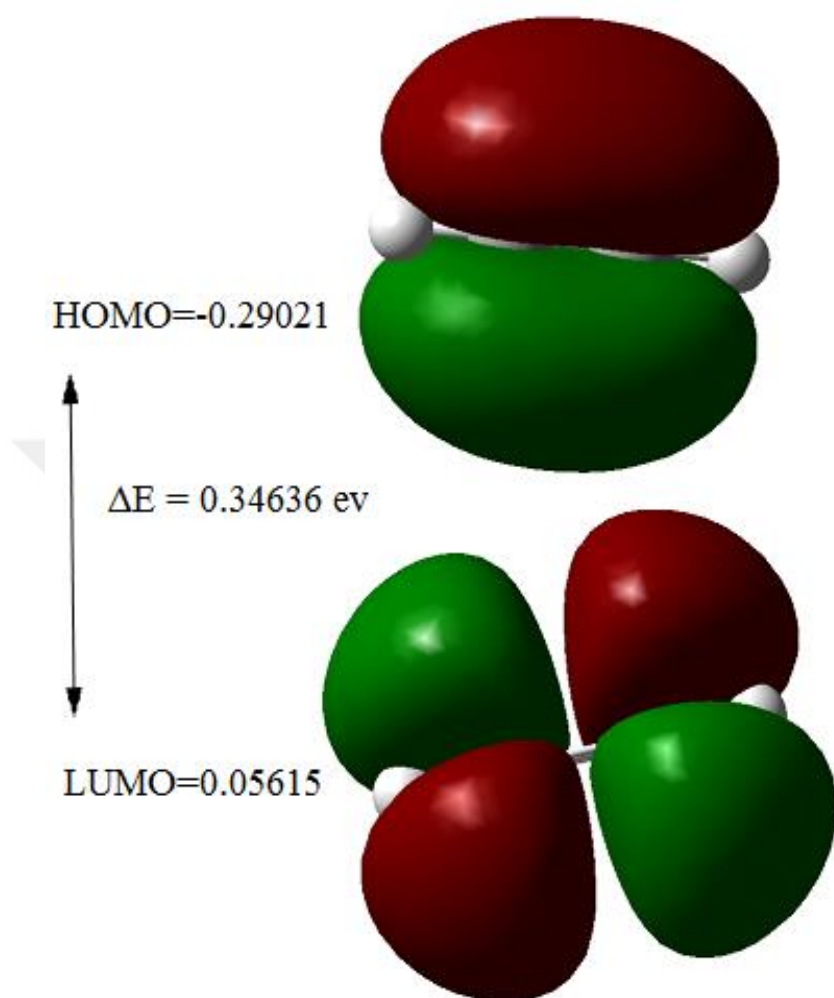


Figure 6. 10. HOMO and LUMO energies of C₂H₂ molecule.

The HOMO and LUMO values for the C₂H₂ molecule are -0.29021 eV and 0.05615 eV respectively. The energy band gap between HOMO and LUMO is 0.34636 eV as shown Figure 6.10. This value is a band gap energy for the ethyne molecule.

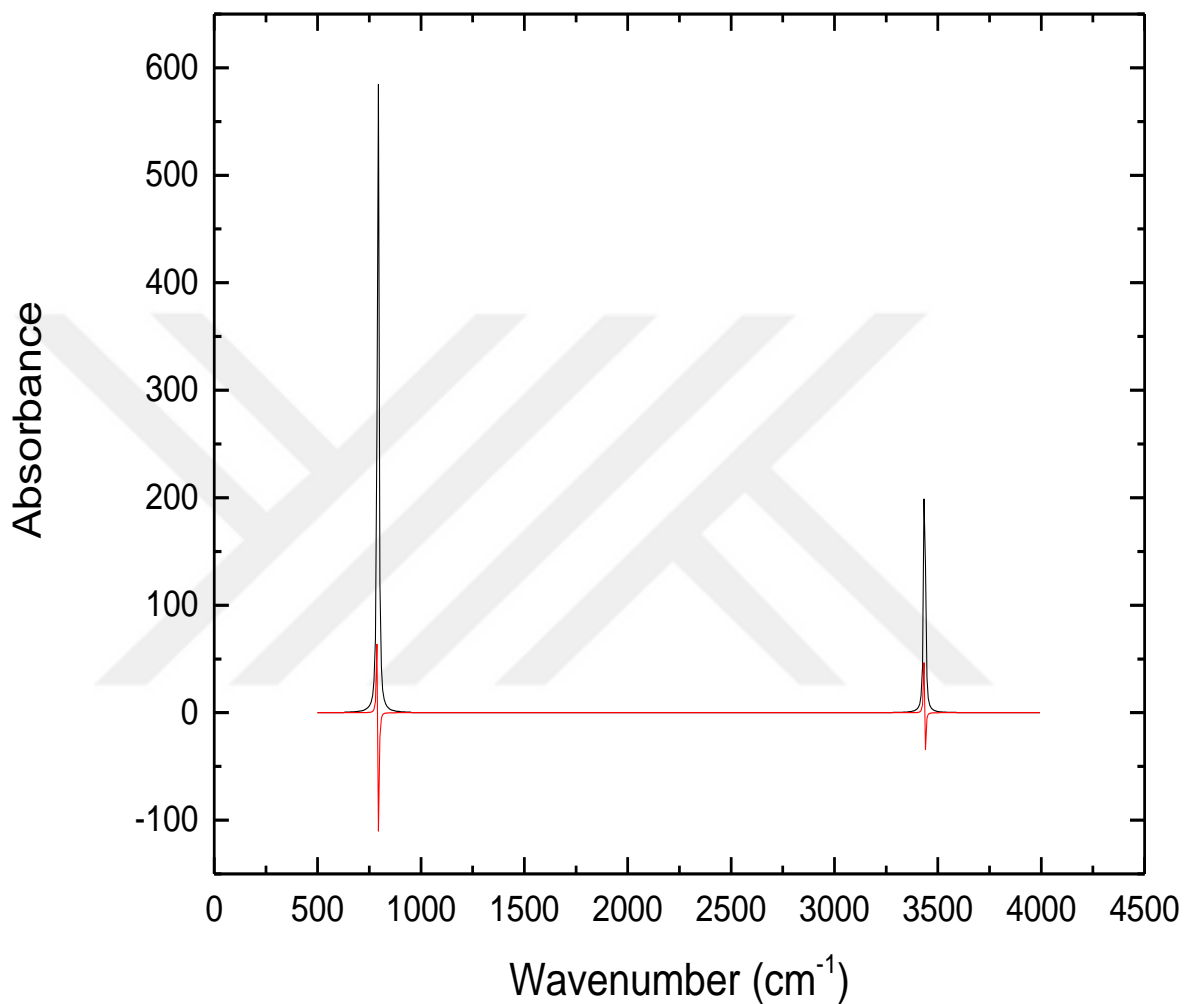


Figure 6. 11. FTIR spectroscopy results for the C₂H₂.

Figure 6.11 is the FTIR spectrum of the ethyne molecule that has been studied in this thesis. This figure is obtained from the frequency calculations of DFT method. As it can be seen from the figure there are two sharp pick. These picks are corresponded to the vibration modes of the C₂H₂ molecule.

6.4. Propane Molecule

Figure 6.12 displays the symbolic optimized structure of propane molecule. For this molecule, we implement DFT method with a 6-311G basis set to calculate quantum quantities. Vibration modes of the title molecules have calculated by implementing DFT method which gives us the infrared information about the molecular systems.

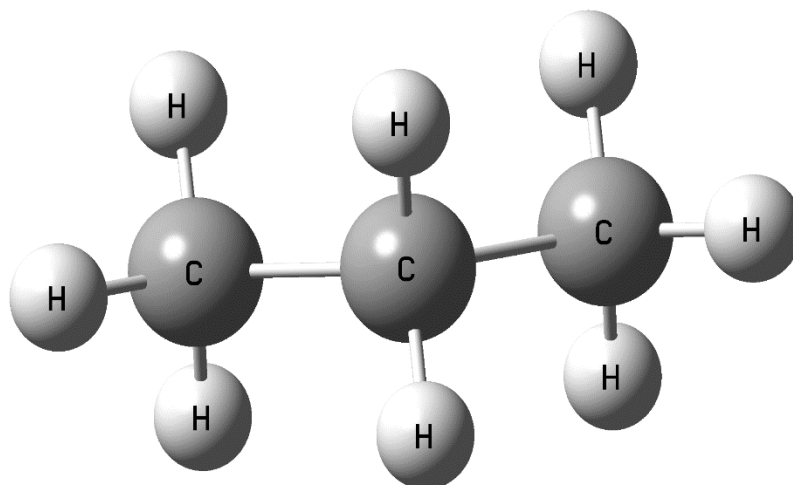


Figure 6. 12. Atomic symbolic structure for the C_3H_8 (Propane) molecule.

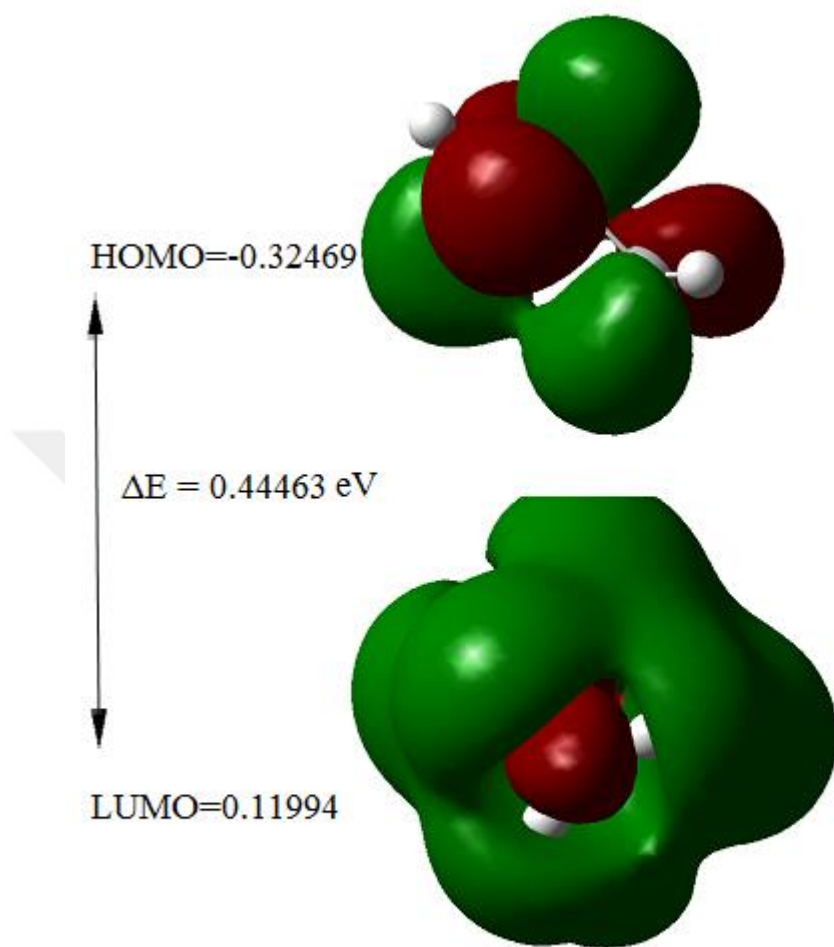


Figure 6. 13. HOMO and LUMO energies of the C₃H₈ molecule.

The HOMO and LUMO values for the C₃H₈ molecule are -0.32469 eV and 0.11994 eV respectively. The energy band gap value between HOMO and LUMO was calculated as shown in Figure 6.13 to be of 0.44463 eV.

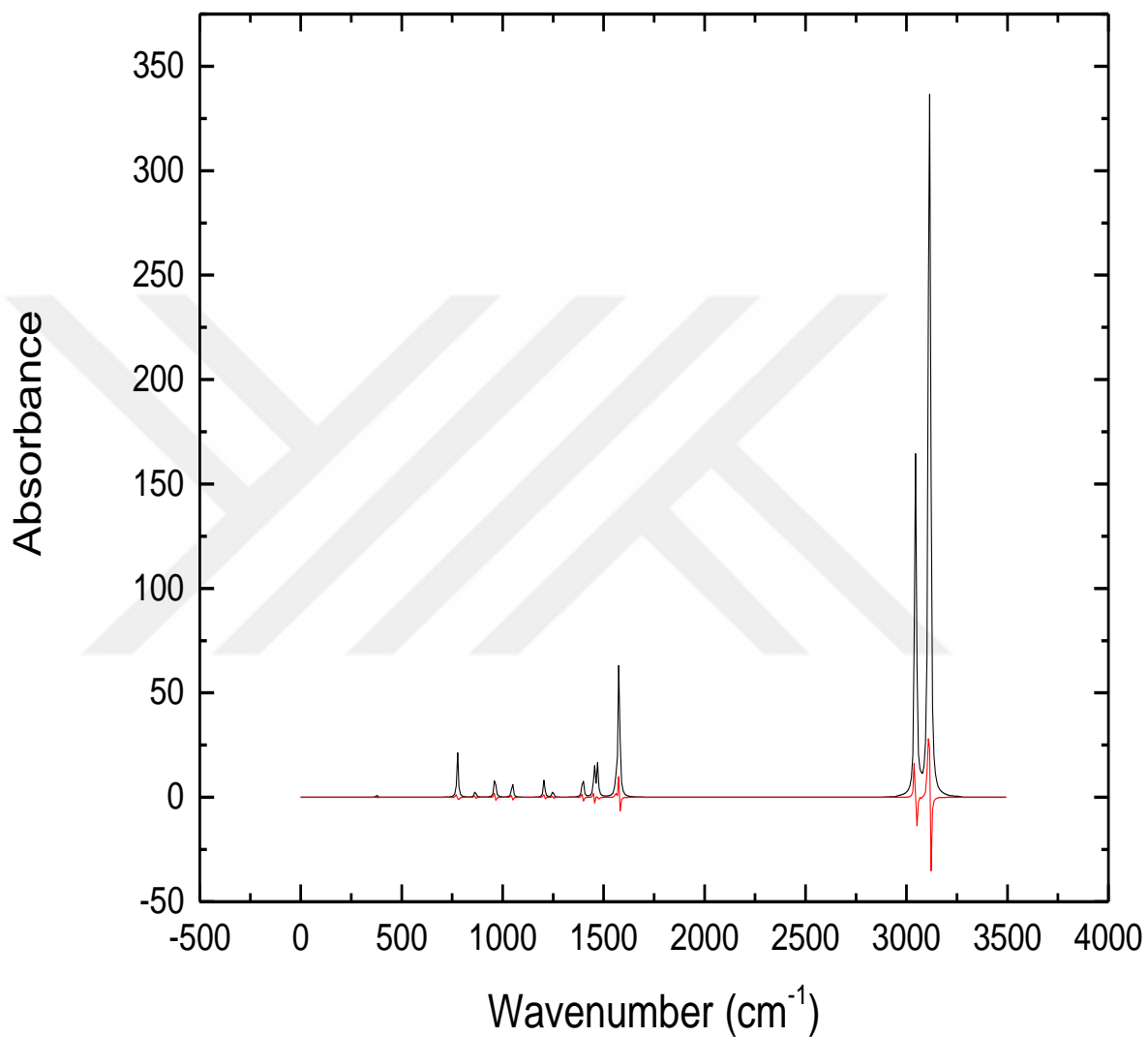


Figure 6. 14. FTIR spectroscopy results for the C₃H₈.

Figure 6.14 is the FTIR spectrum of the propane (C₃H₈) molecule that has been studied in this thesis. This figure is obtained from the frequency calculations of DFT method. As it can be seen from the figure there have been some picks. These picks corresponded to the vibration modes of the propane molecules. This molecule has a big vibration motion at around 3000 cm⁻¹ wavenumbers.

6.5 Nitrous Acid Molecule

Figure 6.15 displays the symbolic optimized structure of the Nitrous acid molecule. For this molecule, we implement DFT method with a 6-311G basis set to calculate quantum results. With DFT method, we have calculated vibration modes of the title molecules which give us the infrared information about the molecular systems.

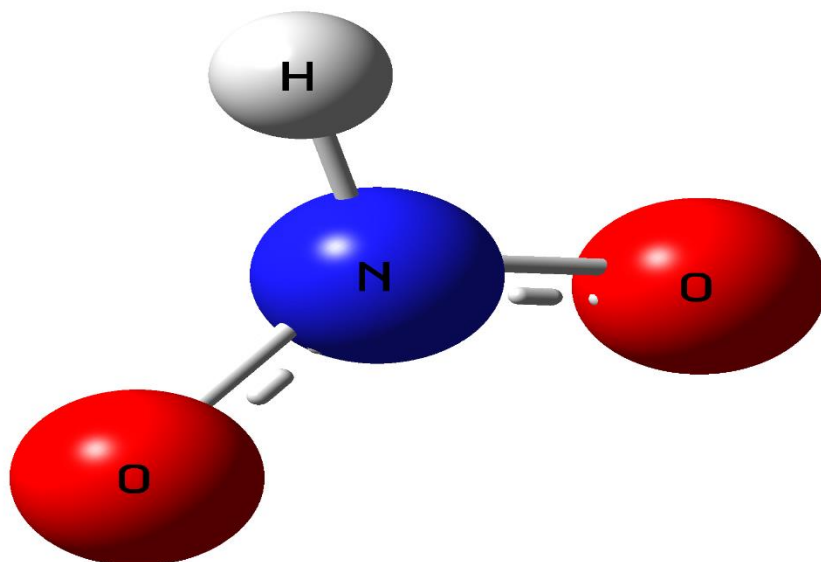


Figure 6. 15. Atomic symbolic structure for HNO₂ (Nitrous acid) molecule.

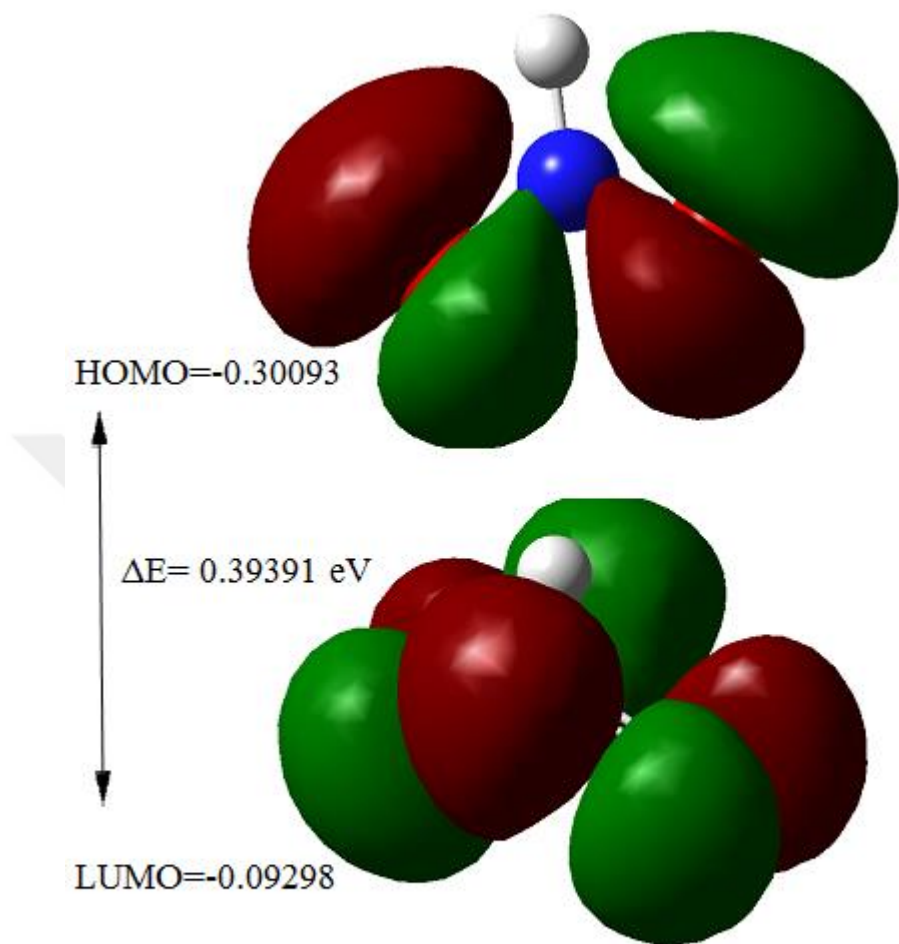


Figure 6. 16. HOMO and LUMO energies of HNO₂ molecule.

The HOMO and LUMO values for the HNO₂ molecule are -0.30093 eV and -0.09298 eV respectively. As can be seen from Figure 6.16 the energy band gap between HOMO and LUMO is 0.39391 eV.

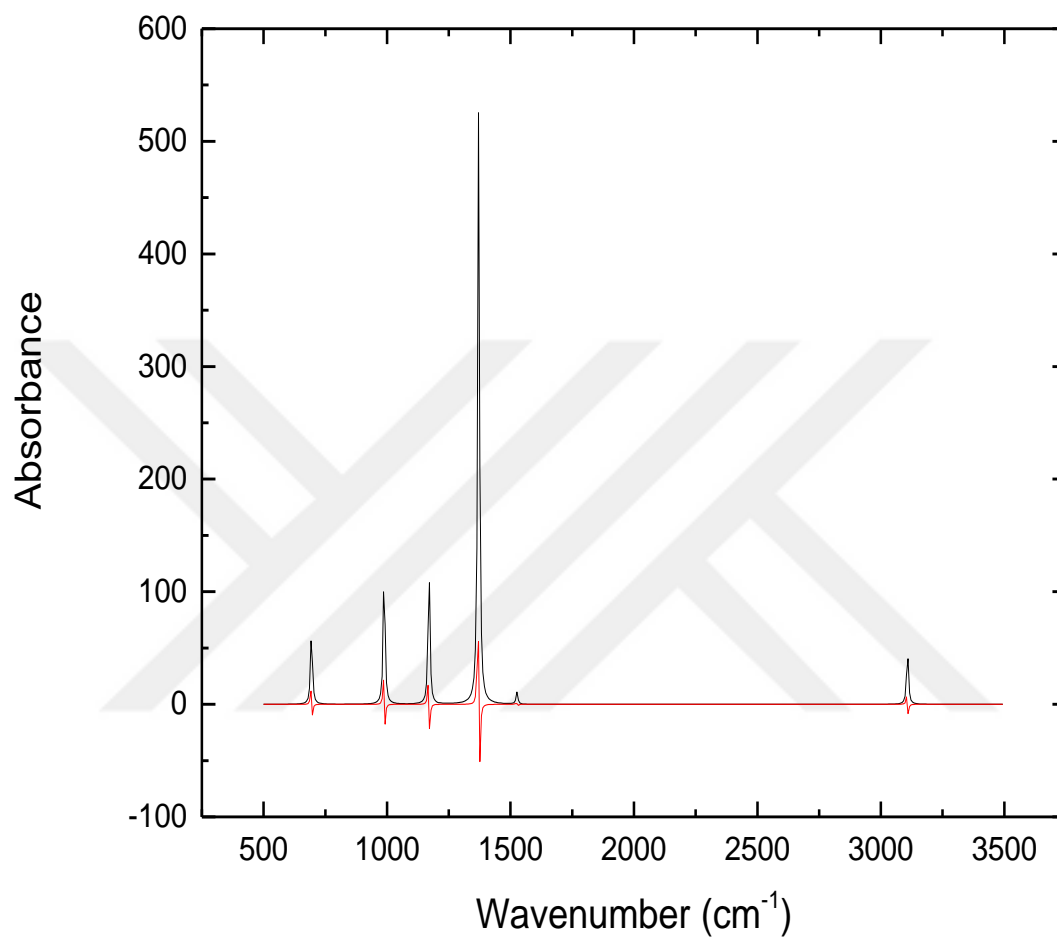


Figure 6. 17. FTIR spectroscopy results for HNO₂.

Figure 6.17 is the FTIR spectrum of the Nitrous acid molecule. This figure is obtained from the frequency calculations of DFT method. As it can be seen from the figure there have been some picks in the lower case of wavenumber. The picks where corresponded to the vibration modes of the studied molecules.

6.6. Water Molecule

Figure 6.18 displays the symbolic optimized structure of water molecule. For this molecule, we implement DFT method with a 6-311G basis set to calculate quantum results. With DFT method, we have calculated vibration modes of the title molecules which give us the infrared information about the molecular systems.

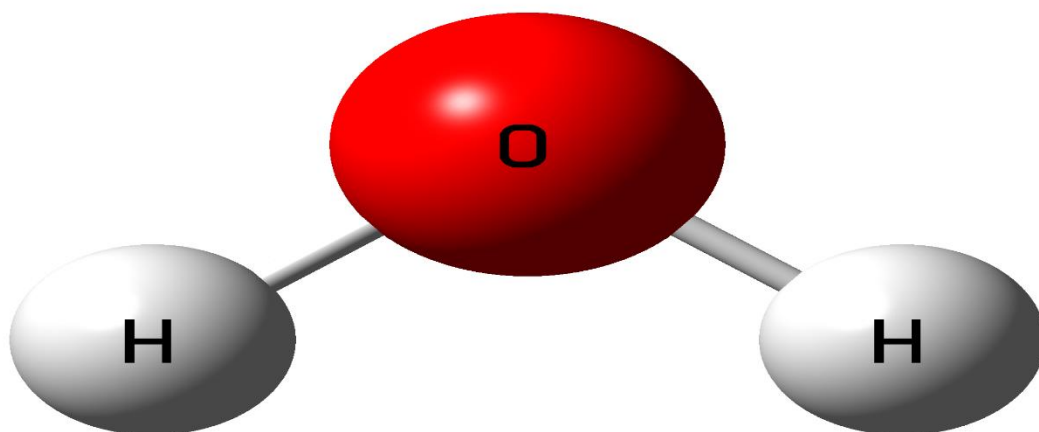


Figure 6. 18. Atomic symbolic structure for H₂O (Water) molecule.

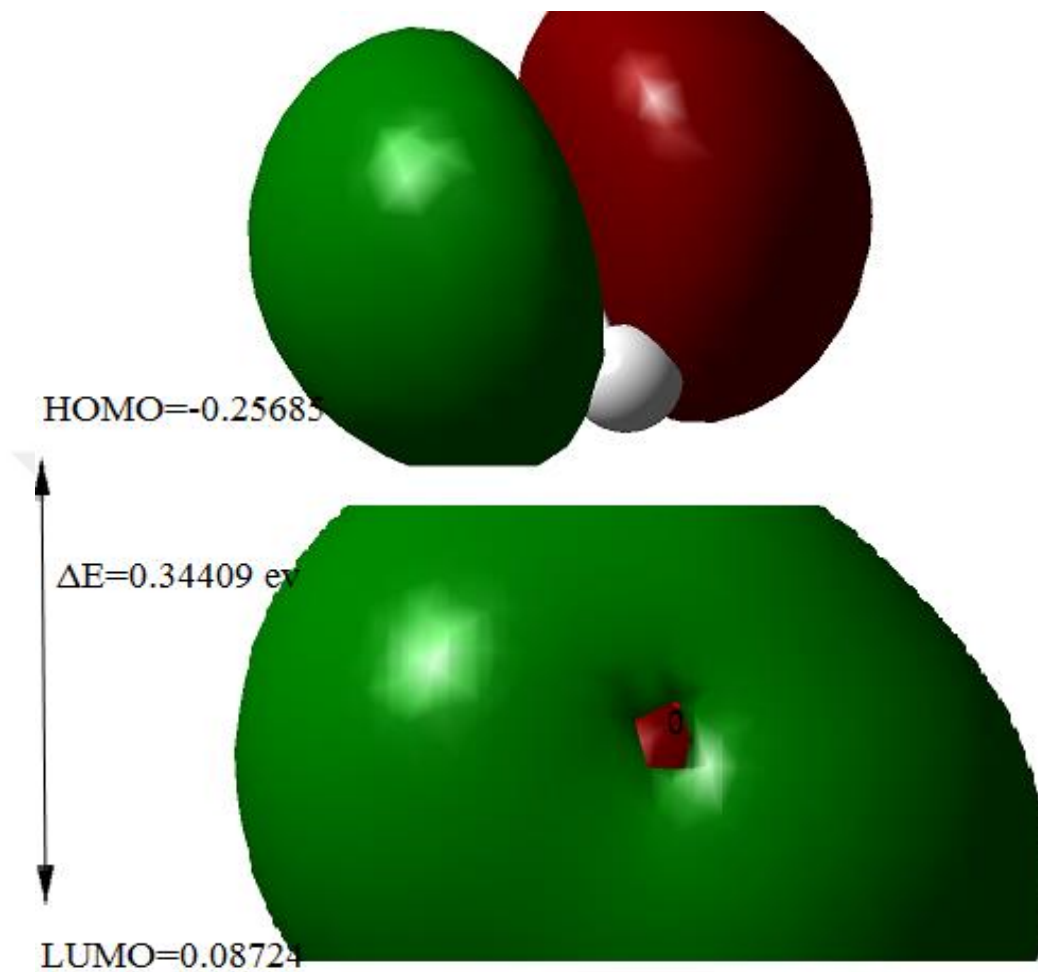


Figure 6. 19. HOMO and LUMO energies of H₂O molecule.

The HOMO and LUMO values for the H₂O molecule are -0.25685 eV and 0.08724 eV respectively and depicted in Figure 6.19. The energy band gap between HOMO and LUMO calculated as 0.34409 eV.

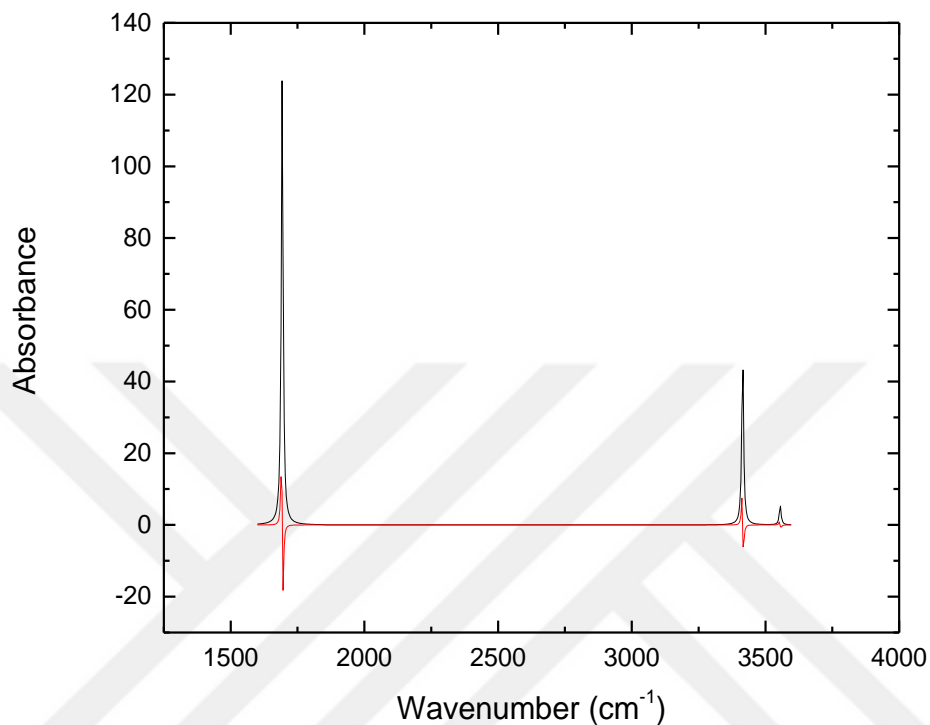


Figure 6. 20. FTIR spectroscopy results for H₂O.

Figure 6.20 is the FTIR spectrum of the H₂O molecule. This figure is also obtained from the frequency calculations of DFT method. Water molecule has some vibration in lower and higher values of wavenumbers. These picks are corresponded to the vibration modes of the studied molecules.

The band gap energy values for the C₂H₂ molecule is 0.34636 eV, for the C₃H₈ is 0.44463 eV, for the HNO₂ is 0.39391 eV and for the H₂O is 0.34409 eV. As can be seen from these values the band gap has chance depending of the molecule.

As results in this thesis, we have calculated electron densities, FTIR spectrums, HOMO and LUMO energy values for Naphthalene, C₂H₄, C₂H₂, C₃H₈, HNO₂, H₂O molecules. It was found that the number of picks for Naphthalene is larger than the C₂H₄ molecule and the others which are depending on the vibration modes of the systems. We also have calculated the HOMO and LUMO energy levels of all the molecules [33-36].

7. REFERENCES

- [1] **Stuart, B.** (2005). *Infrared spectroscopy*. John Wiley & Sons, Inc.
- [2] **Brand, L., & Witholt, B.** (1967). [87] Fluorescence measurements. *Methods in Enzymology*, 11, 776-856.
- [3] **Chalmers, J. M., & Griffiths, P. R.** (2002). Vibrational Spectroscopy: Sampling Techniques and Fiber-Optic Probes. *Handbook of Vibrational Spectroscopy*.
- [4] **Ulman, A.** (2013). *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly*. Academic press.
- [5] Biophysics Department of the University of Kassel. Infrared Spectroscopy. [Online]. Available at: http://www.membranproteine.net/Chapter%202_IR.pdf (Accessed on 22 Oct.2016).
- [6] **Schmitt, J., & Flemming, H. C.** (1998). FTIR-spectroscopy in microbial and material analysis. *International Biodeterioration & Biodegradation*, 41(1), 1-11.
- [7] Materials science. Spectroscopy. 2008. [Online]. Available at: https://www.cs.mcgill.ca/~rwest/link-suggestion/wpcd_2008_09_augmented/wp/s/Spectroscopy.htm (Accessed on 22 Oct.2016).
- [8] **Taillandier, E., & Liquier, J.** (1992). [16] Infrared spectroscopy of DNA. *Methods in enzymology*, 211, 307-335.
- [9] **Morozhenko, V. (Ed.)**. (2012). *Infrared Radiation*. InTech.
- [10] **Stuart, B. H.** (2004). Biological applications. *Infrared spectroscopy: fundamentals and applications*, 137-165.
- [11] **Lu, Y., Ling, Y. S., Wu, H. P., & Li, X. X.** (2004). Study on Passive Distance Measurement of Ground Objects by Infrared Radiation [J]. *Journal Infrared Millimeter and Waves*, 1, 016.

- [12] Cook, P. J., Shergold, J. H., & Cook, P. J. (2005). *Phosphate Deposits of the World: Volume 1: Proterozoic and Cambrian Phosphorites*. Cambridge University Press.
- [13] **Hug, S. J.** (1997). In Situ Fourier Transform Infrared Measurements of Sulfate Adsorption on Hematite in Aqueous Solutions. *Journal of Colloid and Interface Science*, 188(2), 415-422.
- [14] **Brisdon, A. K.** (1998). Inorganic spectroscopic methods. *Oxford chemistry primers*, 62(1), ALL-ALL.
- [15] **Instituto de Física de São Carlos.** Infrared Spectroscopy. [Online]. Available at: <http://www.ifsc.usp.br/~lavfis2/BancoApostilasImagens/ApLuminescencia/Infrared%20Spectroscop1.pdf> (Accessed on 17 Sep. 2016).
- [16] **Siebert, F., & Hildebrandt, P.** **Non-Heme Metalloproteins.** (2008). *Vibrational Spectroscopy in Life Science*, 283-303.
- [17] **Wilson, E. B., Decius, J. C., & Cross, P. C.** (2012). *Molecular vibrations: the theory of infrared and Raman vibrational spectra*. Courier Corporation.
- [18] **Herzberg, G.** (2013). *Molecular spectra and molecular structure* (Vol. 1). Read Books Ltd.
- [19] **Lie Ken Jie, M. S., & Yan-Kit, C.** (1988). The use of a microwave oven in the chemical transformation of long chain fatty acid esters. *Lipids*, 23(4), 367-369.
- [20] **Sholl, D., & Steckel, J. A.** (2011). *Density functional theory: a practical introduction*. John Wiley & Sons.
- [21] **Lima, N. A., Oliveira, L. N., & Capelle, K.** (2002). Density-functional study of the Mott gap in the Hubbard model. *EPL (Europhysics Letters)*, 60(4), 601.
- [22] **Kohn, W.** (1999). Nobel Lecture: Electronic structure of matter—wave functions and density functionals. *Reviews of Modern Physics*, 71(5), 1253.
- [23] **Pople, J. A.** (1999). Nobel lecture: Quantum chemical models. *Reviews of Modern Physics*, 71(5), 1267.

- [24] **Parr, R. G., & Yang, W.** (1989). *Density Functional Theory of Atoms and Molecules* Oxford Univ. Press, New York.
- [25] **Dreizler, R. M., & Gross, E. K. U.** (1990). *Density Functional Theory: An Approach to the Quantum Many-Body Problem* Springer.
- [26] **Krieger, J. B., Li, Y., Iafrate, G. J., Gross, E. K. U., & Dreizler, R. M.** (1995). *Density functional theory. Plenum Press, New York*, 191.
- [27] **Hehre, W. J., Shusterman, A. J., & Nelson, J. E.** (1998). *The Molecular Modeling Workbook for Organic Chemistry, Wavefunction. Inc., Irvine, CA, 92612*.
- [28] **Lee, E. C., & MIN, D. B.** (1988). Quenching Mechanism of β -Carotene on the Chlorophyll Sensitized Photooxidation of Soybean Oil. *Journal of Food Science*, 53(6), 1894-1895.
- [29] **Shusterman, A. J., & Shusterman, G. P.** (1997). Teaching chemistry with electron density models. *J. Chem. Educ.*, 74(7), 771.
- [30] **Torrent-Sucarrat, M., Luis, J. M., Duran, M., & Solà, M.** (2001). On the validity of the maximum hardness and minimum polarizability principles for nontotally symmetric vibrations. *Journal of the American Chemical Society*, 123(32), 7951-7952.
- [31] **JUM, A., TAHIR, I., & ARMUNANTO, R.** (2005). In Silico Analysis of Nonlinear Optics Response Property of Several Organic Chromophore Compounds with Semiempirical Method.
- [32] **Hagberg, D. P., Marinado, T., Karlsson, K. M., Nonomura, K., Qin, P., Boschloo, G., ... & Sun, L.** (2007). Tuning the HOMO and LUMO energy levels of organic chromophores for dye sensitized solar cells. *The Journal of organic chemistry*, 72(25), 9550-9556.
- [33] **Hehre, Warren J.** (2003). *A Guide to Molecular Mechanics and Quantum Chemical Calculations*. Irvine, California: Wavefunction, Inc. pp. 85–100.
- [34] **Daintith, J.** (2014). *The facts on file dictionary of inorganic chemistry*. Infobase Publishing.

- [35] **Clark, T., & Koch, R.** (2013). *The Chemist's Electronic Book of Orbitals*. Springer Science & Business Media.
- [36] **Colley, N. D.** (2016). Computational and Experimental Investigations Towards Improving Organic and Dye-Sensitized Semiconductor Solar Cells.

