An investigation of vibrational analysis, thermodynamics properties and electronic properties of Formaldehyde and its stretch by substituent acetone, acetyl chloride and methyl acetate using first principles analysis

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Abstract

This study finds the equilibrium configuration, vibrational analysis, thermodynamic properties, and electronic properties of formaldehyde and its derivatives, namely acetone, acetyl chloride, and methyl acetate, using First Principles Analysis. It emphasizes the impact of substituents on the carbonyl group and the need for this comprehensive analysis. The computational methods employed in this work are Gaussian DFT, GaussSum and Moltran calculations. For formaldehyde, the optimization step starts from the energy of -114.51282 Hartree and gets optimized in the energy -114.5129634 Hartree. Similarly for Acetone, Acetyl chloride and Methyl acetate, optimization step start from -193.74375 Hartree, -613.26 Hartree, -266.805 Hartree and gets optimized in the energy -193.1744033 Hartree, -613.2941798 Hartree, -266.8358066 Hartree respectively. Infrared (IR) spectroscopy is used to analyze vibrational frequencies. The C-H and C=O vibrations are highlighted, showing characteristic peaks for each compound. Heat capacity at constant volume, heat capacity at constant pressure, internal energy, enthalpy, entropy and Gibb's free energy change with change in temperature. Among the derivative of Formaldehyde, Methyl Acetate has the highest energy gap (i.e. 7.4222 eV) and Acetyl Chloride has the small energy gap (i.e. 5.6137 eV). The Chemical parameters like ionization potential, electron affinity, chemical hardness, chemical potential, electronegativity, electrophilicity index, and chemical softness have been also calculated. Electrostatic Potential Surfaces, Molecular Electrostatic Potential, and Electron Density are visualized to understand charge distribution and reactivity regions. Density of State spectra illustrate the density of electron states per unit energy.

Keywords

Density Functional Theory, Electrostatic Potential, HOMO-LUMO, IR spectroscopy, Thermodynamic properties, Density of State.

1 Introduction

Formaldehyde is the first of the series of aliphatic aldehyde. It was discovered by Butlerov in 1859 and has been manufactured since the beginning of the twentieth century. At ordinary temperature Formaldehyde is colorless gas with pungent odor. Because of its relatively low cost, high purity and variety of chemical reactions, Formaldehyde has become one of the world's most important industrial and research chemical. Its biggest use is in the production of industrial resins, urea-formaldehyde, phenol formaldehyde and melamine form aldehyde [1–3]. Formaldehyde (HCHO) is a simple organic compound consisting of a carbon atom bonded to two hydrogen atoms with single bond and an oxygen atom with the carbon atom in the center, forming a carbonyl group (C=O). When the Formaldehyde has its stretch by substituent acetone, acetyl chloride, and methyl acetate, the number of effects on the vibrations, electronic and thermodynamic properties appear on the carbonyl group (C=O). Acetone (CH_3COCH_3) is colorless highly volatile and flammable liquid with pungent ordor. Acetyl Chloride (CH_3COCl) is a reactive and corrosive. Methyl Acetate (CH_3COOCH_3) also known as acetic acid methyl ester or Methyl ethanoate. It is colorless, flammable liquid with a fruity ordor. It is used in Manufacture of flavors, fragrances and pharmaceuticals [4–6]. The presence of the methyl (CH_3) groups on both sides of the carbonyl group forms the Acetone. Acetyl chloride is an acyl chloride, which contains a carbonyl group attached to a chlorine atom. Methyl acetate is an ester, which contains a carbonyl group bonded to an oxygen atom. Gustav E. Lienhard and William P. Jencks investigate the kinetics and mechanisms of thiol addition to carbonyl compounds, forming hemithioacetals and hemithioketals [7]. Carbonyl compounds are commonly found both outdoors and indoors. Their polar nature, stemming from the oxygen atom's high electronegativity, enables a wide range of chemical reactions. Moreover, the presence of substituents and conjugated double bonds further shapes their physical and chemical characteristics [8]. The substituent additivity effects in adiabatic ionization energies imply that cation molecular orbitals are not directly related to those of the neutral molecule [9]. Laurence et al., investigated the impact of substituents on the basicity of carbonyl compounds through various measurements including enthalpy changes in iodine complex formation, solvent sensitivity and carbonyl stretching vibrations. The enthalpic basicity exhibited a strong correlation with protonation scales. The cumulative impact of substituents showed additive effects for enthalpy. The study concluded that inductive effects predominantly influence the basicity of carbonyl groups towards iodine [10].

An investigation that has not been performed previously regarding the equilibrium configuration, vibrational analysis, thermodynamics properties, and electronic properties of formaldehyde and its stretch by substituents acetone, acetyl chloride, and methyl acetate using First Principles Analysis is now essential and important for further study. Therefore, this study aims to gain a deep understanding of the molecular behavior and the effects of substituents on the geometry optimization, vibrational analysis, thermodynamic properties [specific heat capacity at constant volume (Cv), specific heat capacity at constant pressure (Cp), internal energy (U), enthalpy (H), entropy (S) and Gibb's free energy (G) with change in temperature], highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) analysis, Global reactivity descriptor, Electrostatic potential (ESP) surfaces, Molecular Electrostatic Potential (MEP), Electron Density (ED) and density of states (DOS) of formaldehyde and its derivatives, namely acetone, acetyl chloride, and methyl acetate using Density Functional Theory (DFT) with B3LYP/6-$311+G(d',p')$ basis set together with GaussSum 3.0.2 and Moltran. DFT method is used due to their ability to accurately describe molecular structures, vibrational spectra and other different specific characteristics and properties of title molecules. B3LYP is hybrid functional mostly used in DFT and has the exchange correlation energy function in DFT that incorporate a portion of exact exchange from Hartee-Fock theory with the rest of the exchange correlation energy from other sources. It provides accuracy for a wide range of molecular system. $6-311+G(d',p')$ is a basis set relatively large and includes polarization and diffuse function. It allows more accurate representation of electron density around atoms specially for the system with heavy atoms. It is the standard, split valence triple zeta basis set. Its function describes the core and valence orbitals. The core orbital is a contracted Gaussian type orbital made of six Gaussians and the valence orbital is described by two orbitals, one contracted Gaussian type orbital made of three Gaussians and two Gaussian type orbitals. In this study, $6-311G(d',p')$ is 6-311G basis set with added 'd' polarization functions on non-hydrogen atoms and 'p' polrizations for hydrogen. Thus, it also describes a diffuse s and p functions for non-hydrogen atoms. Triple zeta has much finer result than that of double zeta basis sets and is more accurate. Sometimes, Convergence of ab initio results is disappointingly slow with respect to basis set for non-DFT methods. DFT is less dependent on basis set size than wave function based method.

2 Methodology – Computational details

Geometric Optimization is an important in molecular mechanics. It was performed as a first task of the computational work for the formaldehyde and its substitute (Acetone, Acetyle chloride, Methyl Acetate). The optimized geometry, vibrational frequency, HOMO-LUMO analysis and Global reactivity descriptor of given molecules were computed employing the Density Functional Theory (DFT) method using Gaussian 09W software program [11] employing 6-311+G(d$'$,p$'$) basis set based on Becke's three parameter (local, non-local, Hartree-Fock) hybrid exchange functional with Lee- Yang pair correlation functional B3LYP [12,13] at charge value zero. Gaussian calculation is the best prepared using Gauss View 6.0 interface. Gaussian 09W is a general-purpose ab initio electronic structure package which can predict many properties of molecule and reaction pathways based on various uncorrelated and correlated wave function. After processing Gaussian, the .log file and .chk file obtained from Gaussian used to generate various surface representation and to observe various result [14]. The basis set used here is the 6-311+G(d$'$,p$'$) augmented by 'd' polarization functions on heavy atom and 'p' polarization functions on hydrogen atom as well as diffuse function for both hydrogen and heavy atoms [15]. Thermodynamic parameter such as heat capacity at constant volume (Cv), heat capacity at constant pressure (Cp), entropy (S), internal energy (U), enthalpy (H), entrophy (S) and Gibb's free energy (G) were calculated using Moltran software. In addition to this, GaussSum 3.0.2 was used to calculate the density of states (DOS).

3 Results and Discussion

3.1 Geometry Optimization

Geometry Optimization is a method to predict the three-dimensional arrangement of the atoms in a molecules with minimum energy [16]. It is the first task to do while performing the computational work for the given molecules. Figures 1(a) (b) (c) and (d) show the optimized structure, symbol and numbering of atoms of Formaldehyde, Acetone, Acetyl Chloride, Methyl Acetate. Listed Figures 1(a) (b) (c) and (d) are from the DFT calculation and they have their respective total energy versus optimization step number in optimization state. For formaldehyde, the optimization step starts from the energy of -114.51282 Hartree and gets optimized in the energy -114.5129634 Hartree. Similarly for Acetone, Acetyl chloride and Methyl acetate, optimization step start from -193.74375 Hartree, -613.26 Hartree, -266.805 Hartree and gets optimized in the

energy -193.1744033 Hartree, -613.2941798 Hartree, -266.8358066 Hartree respectively [17].

3.2 Vibrational analysis

IR spectroscopy or vibrational spectroscopy is a tool for the measurement of interaction of infrared radiation with matter by absorption, emission or reflection. Basic principle of it states molecules absorb specific frequencies that are characteristics of their structure. The interaction of the matter in infrared radiation signifies the IR spectroscopy and its spectrum shows the relationship between frequency and wave length of the infrared light (transmittance or absorption) [18]. The greater the frequency of oscillation of chemical bond, greater is the wavenumber. By using IR spectrum, it is distinguished that which chemical bond and possible functional group oscillates with how much of specific frequency that corresponds to certain amount of energy.

C-H vibrations

Most organic molecules contain alkane residues and their general appearance can be seen in the infrared spectrum. Figure 2 is the IR spectrum of Formaldehyde and it reveals the presence of H-C-H in-plane scissoring stretching at 2910.1248 cm^{-1}, C-H asymmetric stretching at 1257.5142 cm^{-1}, C-H symmetric stretching at 1528.7213 cm^{-1}, H-C-H out-of-plane wagging at 1190.7995 cm^{-1}. Figure 3 is the IR spectrum for Acetone having C-H asymmetric stretching at 3161.0988 cm^{-1}, H-C-H assymetric stretching at 3105.5663 cm^{-1}, C-H symmetric stretching at 3039.159 cm^{-1}, C-H in-plane scissoring at 1382.2427 cm^{-1} and C-C-C-H in plane rocking at 1234.2899 cm^{-1}. Figure 4 is the IR spectrum of Acetyl Chloride, having C-H asymmetric stretching at 3331.3231 cm^{-1} and 2201.8905 cm^{-1}, C-C-H in-plane rocking at 282.2516 cm^{-1}. Figure 5 is the IR spectrum of Methyl Acetate having C-H asymmetric stretching at 3179.0767 cm^{-1}, 3122.3869 cm^{-1}, 3041.8403 cm^{-1}, H-C-H in-plane scissoring at 1393.9274 cm^{-1}, H-C-H out-of-plane wagging at 999.1881 cm^{-1}.

C=O vibrations

The carbon-oxygen double bond formed by $\pi - \pi$ between carbon and oxygen, and the lone pair of electrons on oxygen also determines the nature of carbonyl group. The C=O stretching is a characteristic wavenumber of carboxylic acid. The carbonyl C=O stretching vibrational mode is expected to occur in the region 1680–1715 cm^{-1}. Figure 2 is the IR spectrum of Formaldehyde and it shows C=O stretching at 1816.9839 cm^{-1}. Figure 3 is the IR spectrum for Acetone and it has C=O stretching at 1789.4345 cm^{-1}. In figure 4, spectrum for C=O stretching at 1747.0313 cm^{-1} is obtained for Acetyl Chloride. Figure 5 is the IR spectrum of Methyl Acetate showing C=0 stretching at 1821.1828 cm^{-1}.

C-O-C vibration

C-C-O-C in-plane scissoring is observed at 788.341 cm^{-1} and C-O-C stretching at 1089.4461 cm^{-1} for Methyl Acetate is as shown in figure 5.

C-Cl vibrations

Figure 4 shows C-Cl stretching of Acetyl Chloride molecule at 483.3359 cm^{-1}.

Therefore, IR spectroscopy is used for the detailed discussion of structural changes in the given molecule. Structural changes affect their vibrational spectra and provide information about the vibrational modes, vibrational frequencies and intensities of these modes. In a molecule, atoms are connected by chemical bonds, and these bonds have associated vibrational modes. The vibrational frequencies depend on factors such as bond strength, bond length, and mass of the atoms involved. When the structure of the molecule changes, the vibrational modes are influenced due to bond stretch-ing, bending, or the introduction of new functional groups. By analyzing the vibrational spectra of a molecule, we can gain insights into its structure and chemical environment. Changes in vibrational frequencies due to structural modifications can impact the entropy term in the Gibbs free energy equation ($\Delta G = \Delta H - T\Delta S$) and heat capacity of the system. Changes in bond strengths due to alterations in molecular structure affect the enthalpy of a reaction. The enthalpy change (ΔH) is composed of contributions from bond energies and vibrational energies. Stronger or weaker bonds, as indicated by shifts in vibrational frequencies, influence the enthalpy aspects of a chemical reaction. Thermodynamic properties are also connected to the equilibrium constants of reactions. Alterations in molecular structure, reflected in vibrational spectra, can affect the position of equilibrium by influencing the enthalpy and entropy changes.
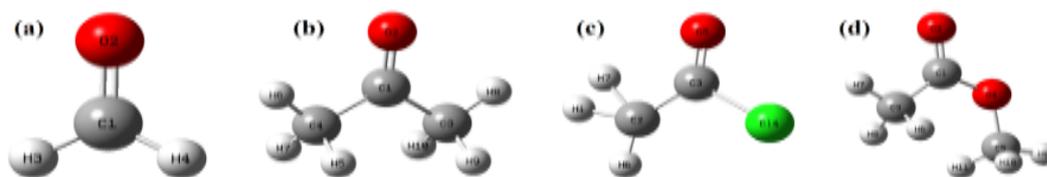
Figure 1: Optimized structure of (a) Formaldehyde (b) Acetone (c) Acetyl Chloride and (d) Methyl Acetate.
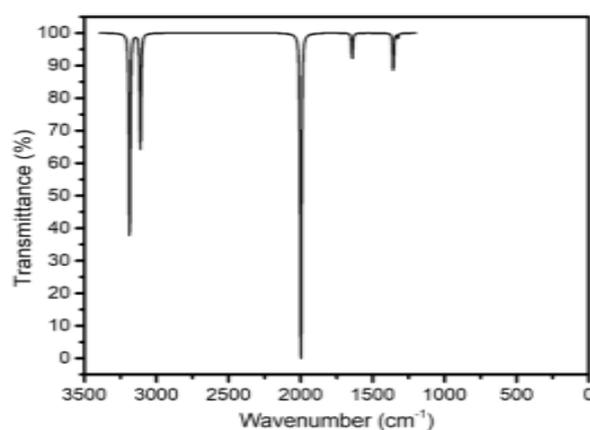
Figure 2: IR spectroscopy for neutral Formaldehyde molecule by DFT method.
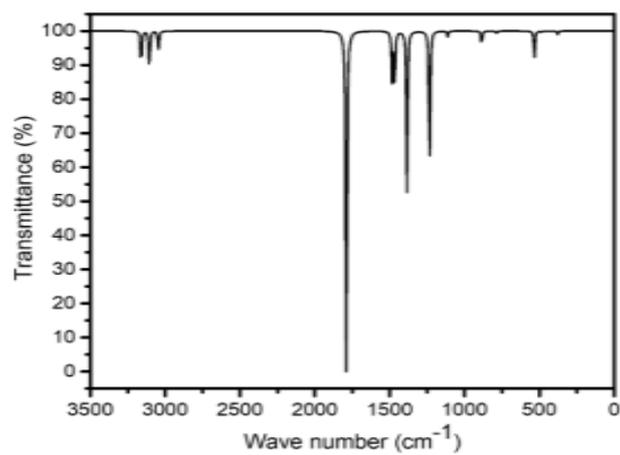
Figure 3: IR spectroscopy for neutral Acetone molecule by DFT method.
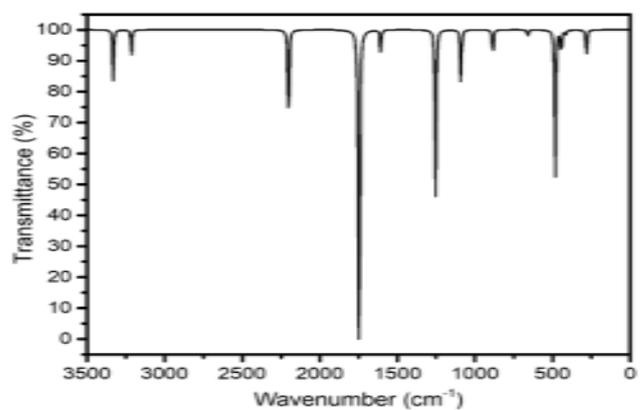
Figure 4: IR spectroscopy for neutral Acetyl Chloride molecule by DFT method.
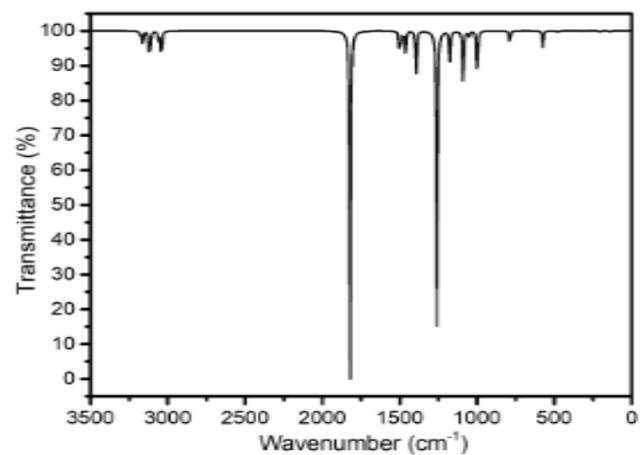
Figure 5: IR spectroscopy for neutral Methyl Acetate molecule by DFT method.

3.3 Thermodynamic analysis

The Formaldehyde, Acetone, Acetyl chloride and Methyl acetate molecules taken for this thermodynamic properties analysis are based on the output file of DFT calculation with B3LYP/6-311+G (d',p') basis set. Moltran software was employed in computing thermodynamic parameters of Formaldehyde, Acetone, Acetyl chloride, Methyl acetate. On the basis of vibrational analysis, the thermodynamic parameter such as entropy (S), enthalpy (H), Gibbs free energy (G), internal energy (U), heat capacity at constant volume (Cv), heat capacity at constant pressure (Cp) were obtained. While performing DFT calculations the molecules was considered to be at room temperature of 298.15 K and one atmospheric pressure. Figures 6, 7, 8 and 9 show the different values of thermodynamic parameters for Formaldehyde, Acetone, Acetyl chloride, Methyl Acetate respectively and these depict the correlation of heat capacity at constant volume (Cv), heat capacity at constant pressure (Cp), internal energy (U), enthalpy (H), entropy (S) and Gibb's free energy (G) with temperature. All the entropies (S) for all the given molecules sharply increase from 10 K to 50 K and decreases the increase in rate from 50 K to 500 K. Parameters such as Cv, Cp, U and H except G increase relentlessly with temperature going from 10 K to 500 K. These increase in thermodynamic parameters are due to enhancement of the molecular vibration intensities with increment in temperature. However, G in all the Figures 6, 7, 8, and 9 decrease with increase in temperature. It is because of the G depends upon the S and as the S increases G decreases [19]. S changed shows that the atom has greater adaptability of changing its own thermodynamic system regarding the temperature [20]. The G represents the energy that is free to do useful work for spontaneous process. The S and H changes revealed that the tittle compound possess more flexibility of changing its own thermodynamic system with respect to the temperature.
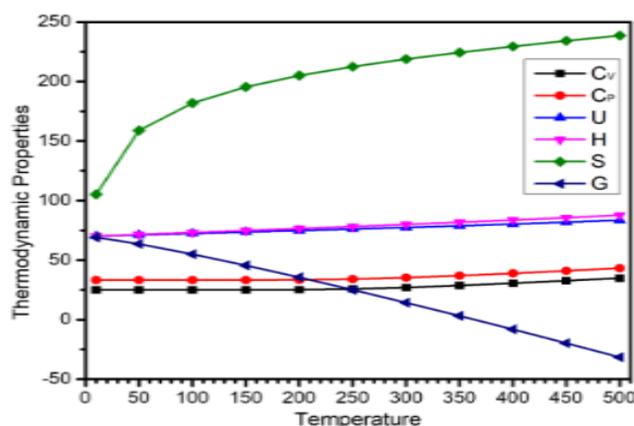
Figure 6: Correlation plot of the thermodynamic properties at different temperature of the Formaldehyde.
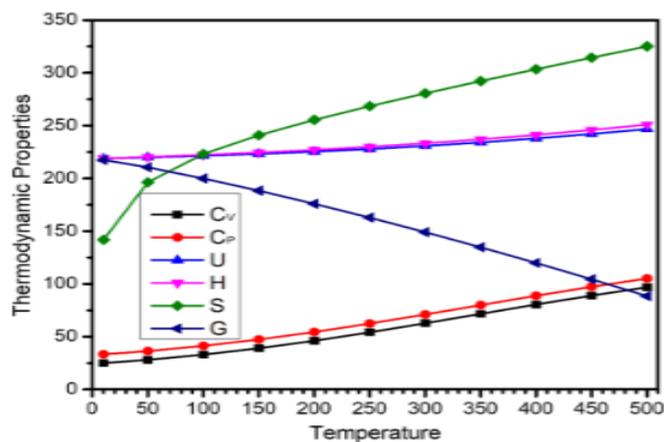
Figure 7: Correlation plot of the thermodynamic properties at different temperature of the Acetone.
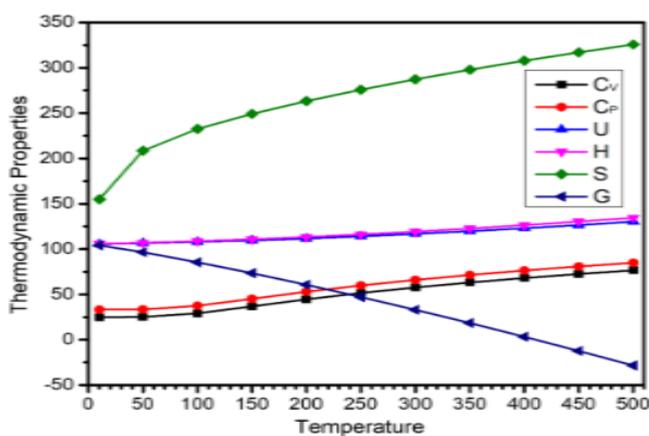
Figure 8: Correlation plot of the thermodynamic properties at different temperature of Acetyl Chloride.
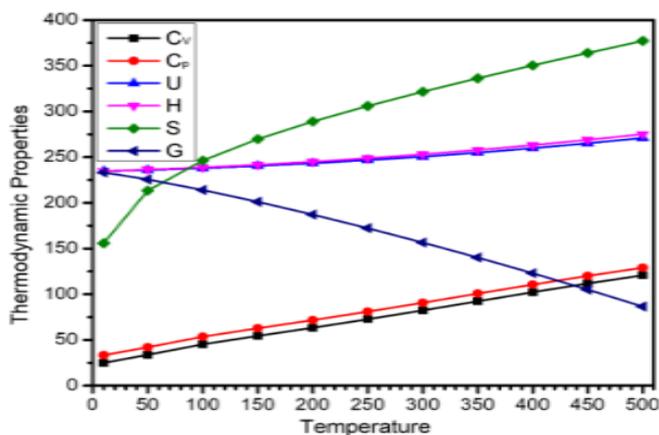
Figure 9: Correlation plot of the thermodynamic properties at different temperature of the Methyl Acetate.

3.4 HOMO-LUMO analysis

The electronic transition corresponds from HOMO (characterizes of electron giving) to the LUMO (characterizes of the electron accepting) orbitals. Both the frontier molecular orbitals (FMOS) (i.e. HOMO and LUMO) are the main orbitals taking part in the chemical reaction [21]. High value of HOMO energy is likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy. The lower value of the LUMO energy shows more probability to accept electrons. The energy of the HOMO is directly related to the ionization potential and the energy of the LUMO is directly related to the electron affinity. So, the energy gap difference between the HOMO and LUMO is an important stability index. A higher value of the energy difference is the stability of the molecular system. Low gap value refers the higher electron transition and vice versa. A large HOMO-LUMO gap implies high stability for the molecule in the sense of its lower reactivity in chemical reaction [22, 23]. The electronic absorption relates to the transition from the ground to the first excited state and mainly described by one electron excitation from HOMO to LUMO [24]. Figures 10(a), (b), (c) and (d) show the three-dimensional plot of the HOMO–LUMO of Formaldehyde, Acetone, Acetyl Chloride and Methyl Acetate molecules using the DFT with B3LYP/6-311+G(d$'$,p$'$) basis set. In the Figure 10(a), it is observed that -7.6708 eV of energy is required to free an electron from formaldehyde molecule and -1.7265 eV amount of energy is released while attaching an electron to neutral atom of formaldehyde. The energy gap between HOMO and LUMO for this Formaldehyde from Figure 10(a) is found to be -5.9443 eV. Figure 10(b) shows that ionization potential of Acetone is -7.0183 eV and electron affinity for Acetone is -0.7371 eV. The calculated energy difference between HOMO and LUMO for Acetone from Figure 10(b) is found to be -6.2812 eV. Similarly, from Figure 10(c), it is observed that -7.0882 eV amount of energy is necessary to release an electron from the highest occupied orbital of Acetyl Chloride and -1.4745 eV energy must release to attach an electron to the lowest occupied molecular orbital of Acetone. From this Figure 10(c), it shows the calculated energy gap of HOMO and LUMO for this Acetyl Chloride compound is -5.6137 eV. Also, Figure 10(d) implies that -7.6379 eV amount of energy is required to free an electron from HOMO of Methyl acetate and -0.2157 eV energy is released while attaching an electron to the LUMO of Methyl acetate. This Methyl Acetate from Figure 10(d) shows the HOMO-LUMO gap -7.4222 eV. In addition to that, it is observed that Methyl acetate has the highest stability implying lower reactivity in the chemical reactions in the sense of its higher energy gap of 7.4222 eV as compared to that of our mother compound formaldehyde (5.9443 eV). On the other hand, Acetyl Chloride molecule is closely stable as Formaldehyde and Acetone is second highest stable compound among the given molecules. Kinetic stability increases with the increase of HOMO-LUMO gap. As a result, removal of electrons from ground state HOMO to excited state LUMO requires more energy.

From the above energy gap, it is clear that the molecule (Formaldehyde, Acetone, Acetyl chloride, Methyl Acetate) under investigation is very soft since it has a small HOMO–LUMO gap.

Global reactivity descriptor

This study introduces a range of chemical reactivity descriptors aimed at enhancing our comprehension of the properties of Formaldehyde, Acetone, Acetyl Chloride, and Methyl Acetate molecules. The ionization potential (IP) and electron affinity (EA) of these compounds were estimated utilizing the calculated HOMO and LUMO energies. Additionally, parameters such as chemical hardness (η), chemical potential (μ), electronegativity (χ), global electrophilicity index (ω) and chemical softness (S) for these molecules have been computed and are presented in Table 1. By using HOMO and LUMO energy values for a molecule, we can calculate the Global reactivity descriptor such as hardness (η), chemical potential (μ), electronegativity (χ), electrophilicity index (ω) and softness (S) using Koopman's theorem for closed-shell molecules [25–27].

The equations (1)–(5) provide the necessary formulas for computing the chemical hardness (η), chemical potential (μ), electronegativity (χ), global electrophilicity index (ω) and chemical softness (S), and they are expressed as follows: The hardness of the moelcule (η) can be expressed as

$$\eta = (I - A)/2 \qquad (1)$$

The chemical potential (μ) of the molecule is the negative of hardness

$$\mu = -(I + A)/2 \qquad (2)$$

The electronegativity (χ) of the molecule is given by the equation

$$\chi = (I + A)/2 \qquad (3)$$

The electrophilicity index (ω) of the molecule is

$$\omega = \mu^2/2\eta \qquad (4)$$

The Softness of the molecule is the reciprocal of hardness

$$S = 1/\eta \qquad (5)$$

where I = - EHOMO called ionization potential and A = - ELUMO called electron affinity. The ionization potential (I) and an electron affinity (A) of Formaldeyde, Acetone, Acetyl chloride, Methyl

acetate are -7.6708 eV, -7.0183 eV, -7.0882 eV, -7.6379 eV and -1.72656 eV, -0.73715 eV, -1.47458 eV, -0.215786 eV respectively. Usually, the compound having higher HOMO-LUMO gap are comparatively harder [28]. The Acetone molecule shows the most hardness (3.140605 eV) in its neutral state. Similarly, it has the most chemical softness $(0.318409 \ (eV)^{-1})$ in its neutral state.

In Table 1, chemical potential is expressed in negative values. Chemical potential measures the potential energy of the substance. A more negative chemical potential suggests a molecule that is more prone to react or release energy. In this context, Acetone has the most negative chemical potential, implying a high reactivity. Methyl acetate has a less negative chemical potential, indicating lower reactivity.

Electronegativity is a measure of the ability of an atom to attract electrons in a chemical bond. From Table 1, Formaldehyde has the highest electronegativity value (4.698725 eV) indicating it has a strong tendency to attract electrons so it is reactive. For Methyl Acetate, it has the lowest electronegativity (0.489788 eV) suggesting it is less inclined to attract electrons. Normally, strong electrophiles have a value greater than 1.5 eV, moderate electrophiles have a value between 0.8 eV and 1.5 eV, and marginal electrophiles have a value less than 0.8 eV [29]. Table 1 shows that the Acetone molecule has strong electrophiles in its neutral state with values of 1.570297 eV and the methyl acetate has the

least electrophiles with the value 0.137800 eV in neutral state indicating marginal electrophiles. The moderate values are found in the Formaldehyde and Acetyl chloride in the neutral state with their values 1.486082 and 1.403425 respectively. Chemical softness is the inverse of global hardness and represents the ease with which a molecule can accept or donate electrons. A higher softness value indicates a molecule's greater responsiveness to electron exchange. From Table 1, Methyl acetate has the highest chemical softness (3.649608 eV) indicating it can more readily engage in electron transfer processes, while Acetone has the lowest chemical softness (0.318409 eV) suggesting it is less responsive to electron exchange.

Reactivity descriptors and thermodynamic parameters are fundamental concepts in understanding chemical reactions and it allows to predict and control reactions, optimize reaction conditions, and design new chemical processes. The global reactivity descriptor associated with the electronic structure principles is also used for analyzing structures, properties, reactivity, bonding, interactions, and dynamics in the context of various physicochemical processes such as molecular vibrations, internal rotations, chemical reaction, stability of isomers, ion-atom collision, atom-filled interactions, solvent effect, etc. Also, global reactivity descriptors such as electronegativity, hardness has a correlation with change in dipole moment which is a measure of ionic character of bond.
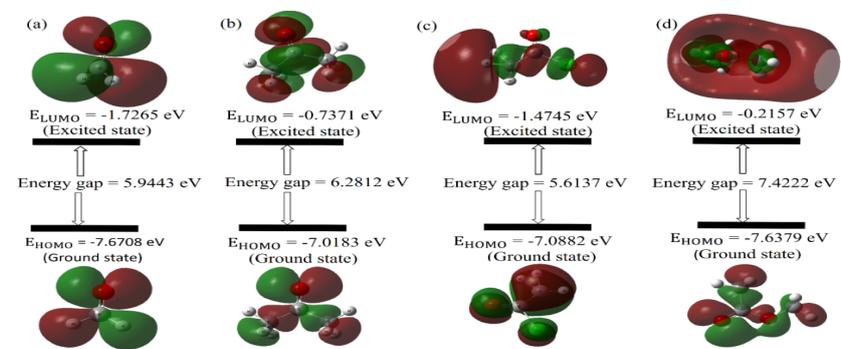
Figure 10: The atomic orbital compositions of the frontier molecular orbital (HOMO-LUMO) by DFT for (a) Formaldehyde (b) Acetone (c) Acetyl Chloride (d) Methyl Acetate.

3.5 Electrostatic potential (ESP) surfaces, Molecular Electrostatic Potential (MEP) and Electron Density (ED)

ESP is used for predicting sites and relative reactivity towards electrophilic attack and for studying of biological recognition and hydrogen bonding interactions and MEP is used as a reactivity map displaying most probable regions for the electrophilic attack of charged point-like reagents on organic molecules [30]. It provides a visual method

to understand the relative polarity of the molecule. One of the most important non-bonded interactions that can be studied with potential maps is the hydrogen bond. ED iso-surface mapped with ESP depicts the size, shape, charge density and site of chemical reactivity of the molecules. Figure 11(a) shows the electrostatic potential (ESP) of the Formaldehyde that ranges from 9.963e-3 to 9.963e-3 a. u. while the Figure 11(b) for molecular electrostatic potential (MEP) i.e. mapped potential

ranges from -4.309e-2 to 4.309e-2 a. u. in its neutral state for the same molecule. Various colors on the surface correspond to distinct electrostatic potential values, which follow a progressive order of increase: from red to orange, then to yellow, green, and finally blue. The chemical reactivity of specific locations is dictated by the molecular electrostatic potential. In this context, the negative regions represented by red and yellow, and are indicative of electrophilic reactivity, while the positive region depicted in blue signifies nucleophilic reactivity [31]. Similarly, ESP of the Acetone ranges from 1.238e-2 to 1.238e-2 a. u. while the mapped MEP ranges from -5.283e-2 to 5.283e-2 a. u. as shown in figure 12(a) and (b). Figure 13(a) and (b) imply the potential of the acetyl chloride ranges from -1.367e-2 to 1.367e-2 and the mapped potential ranges from -9.480e-2 to 9.480e-2 a. u. in neutral state. Likewise, Figure 14(a) and (b) are the electrostatic potential having the ranges from -1.603e-2 to 1.603e-2 and mapped potential with the range from -6.020e-2 to 6.020e-2 a. u. of the Methyl acetate. On comparing both the ESP and MEP of each of the molecule, it is observed that oxygen atom is mostly tilting towards the negative potential and rest of the region is mostly feasible to the zone of positive potential. From all the Figures of 11(a) (b), 12(a) (b), 13(a) (b), and 14(a) (b), we can see that the highest electronegativity is located in the carboynl group. The MEP of each title molecule from Figure 11(b), 12(b), 13(b) and 14(b) clearly demonstrates the present of a hydrogen atom has the most positive electrostatic potential which can be considered as possible sites for nucleophilic attack. For ESP of figure 11(a), 12(a), 13(a) and 14(a), the negative potential is localized near Oxygen due to the more electrophilic attack (red and yellowish region), while the positive potential is localized on the rest surface indicating nucleophilic attack. Regarding the ED plot of the Formaldehyde, Acetone, Acetyl Chloride and Methyl Acetate from the Figure 11(c), 12(c), 13(c) and 14(c) using DFT method of calculation, these show uniform charge distribution and the probability of an electron being present at the specific location.

Table 1: Global Reactivity Descriptors of Formaldehyde, Acetone, Acetyl Chloride, and Methyl Acetate molecules in neutral state.

Property	Energy (eV) values of different molecules			
	Formaldehyde	Acetone	Acetyl Chloride	Methyl Acetate
Global Hardness (η)	2.972165	3.140605	2.806855	0.274002
Chemical potential (μ)	-2.972165	-3.14060	-2.806855	-0.274002
Electronegativity (χ)	4.698725	3.877755	4.281435	0.489788
Global Electrophilicity (ω)	1.486082	1.570297	1.403425	0.137800
Chemical Softness (S)	0.336455	0.318409	0.356270	3.649608
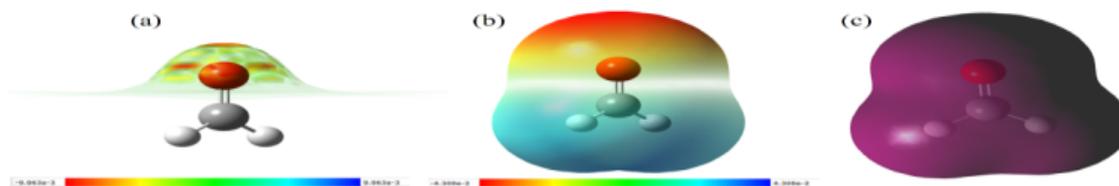
Figure 11: (a) ESP (b) MEP (c) ED by DFT for Formaldehyde.
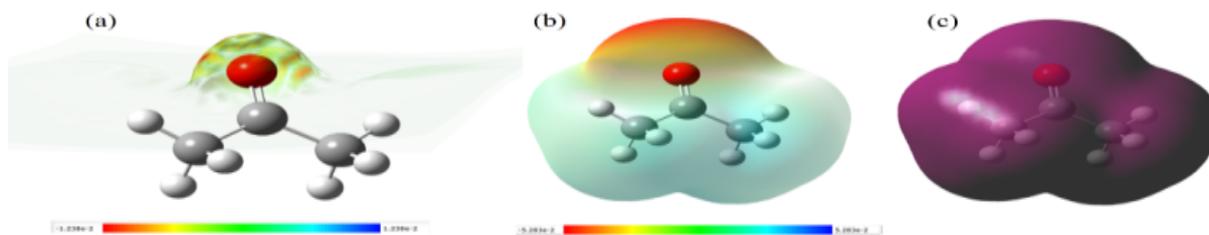
Figure 12: (a) ESP (b) MEP (c) ED by DFT for Acetone.
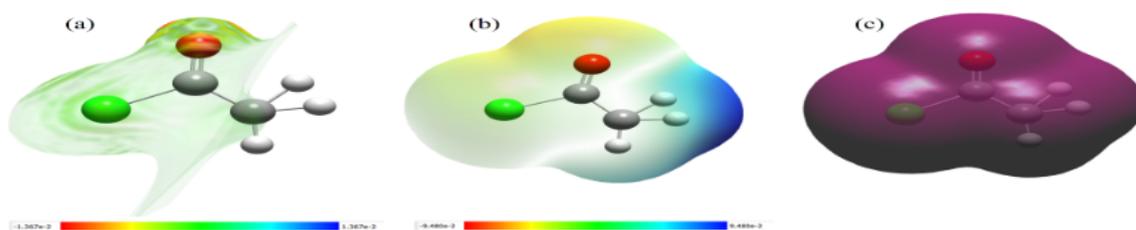
Figure 13: (a) ESP (b) MEP (c) ED by DFT for Acetyl Chloride.
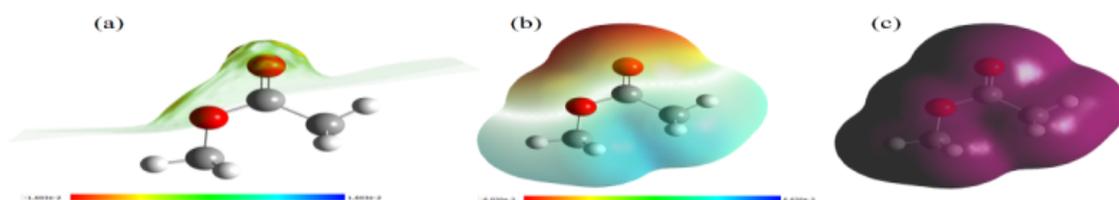
Figure 14: (a) ESP (b) MEP (c) ED by DFT for Methyl Acetate.

3.6 Density of state (DOS)

The consideration of only HOMO and LUMO may not provide a realistic description of the frontier orbitals, it is because of the neighboring orbitals may show quasi-degenerate energy levels in the boundary regions [31, 32]. For this reason DOS has been calculated using GaussSum 3.0.2 program. The most important application of the DOS plot is to demonstrate the MO composition and their contributions to the chemical bonding through positive and negative charges [33]. The plot reveals to determine whether the interaction between two orbitals is of a bonding or anti-bonding nature. When the DOS exhibits a high intensity at specific energy lev-

els, it signifies the presence of numerous available states for occupation. Conversely, a zero intensity indicates the absence of available states, while a negative intensity signifies an anti-bonding interaction [34]. In addition to this, he energy values presented in the HOMO-LUMO analysis also align well with the energy gap depicted in the DOS spectrum. Figure 15 represents the DOS plot for highest and lowest energy gap of the Formaldehyde and its derivatives in the energy range from – 20 eV to 0 eV and with a full width at half maximum (FWHM) of 0.3 eV. In Figure 15(a), the energy gap from DOS spectrum (i.e. 5.9176 eV) is lower than 5.9443 eV for FMO of formaldehyde and it means that there are only (5.9176 eV) states available for

occupation. Figure 15(b) shows that Acetone has 6.2825 eV number of electron state per unit volume per unit energy which is very much close to energy gap (6.2812 eV) obtained from FMO's of Acetone. Similarly, figure 15(c) is the DOS for Acetyl Chloride having 5.6233 eV unit energy per unit volume which is a little higher than energy gap (5.6137 eV) obtained from FMO's of Acetyl Chloride. In figure 15(d), it is found that DOS for Methyl Acetate having 7.1838 eV unit energy per unit volume which is

less than the energy gap obtained (7.4222 eV) from FMO's of Methyl Acetate. The energy values presented in the HOMO-LUMO analysis are well coordinated with the energy gap depicted in the DOS spectrum. DOS spectrum for HOMO and LUMO in figure 15 for formaldehyde and its substitutions shows exact stability of given compounds and found that Methyl Acetate is most stable due to O–C=O group present in it.
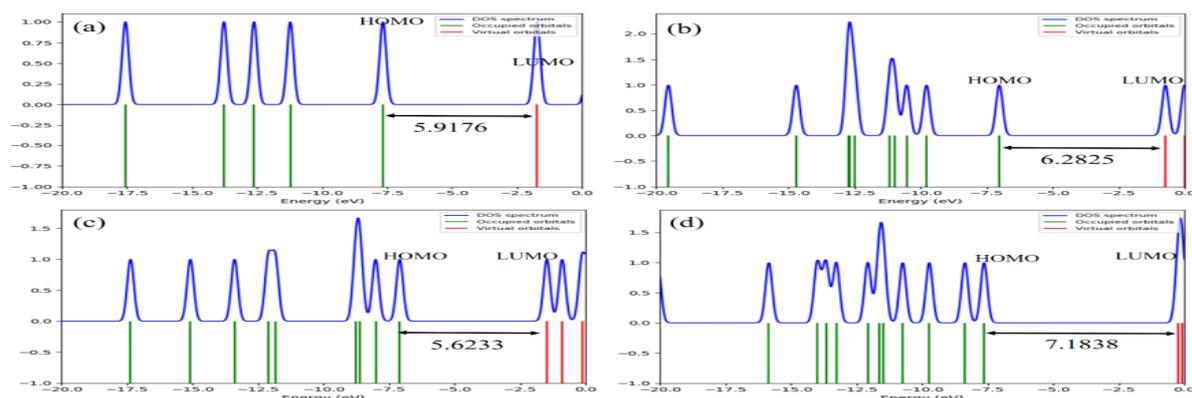
Figure 15: DOS spectrum of (a) Formaldehyde (b) Acetone (c) Acetyl Chloride (d) Methyl Acetate at B3LYP with basis set 6-311+G(d$'$,p$'$).

4 Conclusion

This study conducted an in-depth analysis of the molecular properties of Formaldehyde, Acetone, Acetyl Chloride, and Methyl Acetate using various computational methods. Gaussian calculations were conducted using the DFT method with the 6-311+G(d$'$,p$'$) basis set in which the optimization process successfully minimized the energy for each molecule. Infrared (IR) spectroscopy analyzed the vibrational modes of the molecules in which specific vibrational frequencies corresponding to C-H, C=O, C-O-C, and C-Cl bonds were identified. Thermodynamic parameters such as entropy, enthalpy, Gibbs free energy, internal energy, heat capacity at constant volume, and heat capacity at constant pressure were computed and the data showed how these parameters varied with temperature and provided insights into the thermodynamic behavior of the molecules. Frontier molecular orbitals (HOMO and LUMO) were analyzed to understand the electronic structure and reactivity of the molecules. The energy gap between HOMO and LUMO was used as an indicator of molecular stability. Methyl Acetate was found to be the most stable molecule due to its higher HOMO-LUMO energy gap. Chemical reactivity descriptors, including ionization potential, electron affinity, chemical hardness, chemical potential, electronegativity, electrophilicity index, and chemical

softness, were calculated to assess the reactivity of the molecules. Acetone exhibited strong electrophilic reactivity, while Methyl Acetate had the lowest reactivity. Electrostatic potential maps were generated to visualize the polarity and reactivity of the molecules. Negative potential regions indicated electrophilic sites, while positive potential regions suggested nucleophilic sites. The electron density plots showed uniform charge distribution within the molecules. DOS spectra were used to analyze the molecular orbitals and their contributions to chemical bonding. The energy gaps obtained from DOS analysis aligned well with the HOMO-LUMO energy gaps, providing further validation of the molecular stability rankings. The comprehensive computational analysis provided a detailed understanding of the structural, vibrational, electronic, thermodynamic, and reactivity properties of Formaldehyde, Acetone, Acetyl Chloride, and Methyl Acetate.

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