Journal of Modeling and Simulation of Materials
ISSN: 2582-2365
Volume 7, Issue 1, pp. 1-17, 2025
DOI: https://doi.org/10.21467/jmsm.7.1.1-17

RESEARCH ARTICLE

Detection of Tetrachlorobutadiene Isomers Using Density Functional Theory Methods: A Comparative Study of Hartree-Fock and Density Functional Theory Analysis

Kaniz Fatema

Chemical and Molecular Engineering Department, Stony Brook University, New York, USA

*Corresponding Author's e-mail: fatemache10@gmail.com

Received: 11 September 2024 / Revised: 27 September 2024 / Accepted: 21 December 2024 / Published: 04 February 2025

ABSTRACT

The study aims to build upon previous research by incorporating Density Functional Theory (DFT), specifically using the B3LYP functional, to improve the computational methodology for analyzing chlorobutadiene (TCBD) compounds. DFT is chosen for its ability to account for electron correlation effects beyond the mean-field approximation, a limitation found in earlier approaches such as the Hartree-Fock (HF) method. By incorporating electron correlation, DFT provides a more accurate description of molecular properties, making it highly suitable for analyzing complex molecular structures like those found in chlorobutadienes. The methodology adopted in the study comprises four key steps. First, the molecular structure of each isomer was created. Next, the geometry of the isomers was optimized using DFT methods to ensure the most stable configurations for further analysis. The third step involved computing the vibrational frequencies of the molecules using the B3LYP functional, with different basis sets applied depending on the isomer under study. Finally, the simulated infrared (IR) spectra generated through DFT were compared with existing data from the literature to validate the findings and assess the accuracy of the computational model. The study focuses on nine different Tetrachlorobutadiene (TCBD) isomers, each with unique configurations of hydrogen and chlorine atoms. These structures were visualized using Molden software, and the IR spectra for each isomer were obtained using DFT, specifically the B3LYP and B3LYP-D3BJ functionals. The analysis of the IR spectra revealed characteristic peaks corresponding to various functional groups within the TCBD molecules. Notable vibrational modes include C-Cl stretching, C=C stretching and bending, and C-H stretching and bending, which are essential in identifying the chemical composition of the isomers. A comparative analysis was conducted between DFT and the previously employed Hartree-Fock (HF) method. The results clearly showed that DFT was more efficient in identifying functional groups within the TCBD isomers. DFT provided IR spectra with well-defined peaks that were consistent across all isomers, offering a more detailed and accurate molecular analysis. In contrast, the HF method, while capable of detecting some functional groups, was less consistent and notably missed certain peaks, particularly in the C-H stretching region. This demonstrates the flexibility and superior accuracy of DFT, making it a more reliable tool for molecular structure analysis, especially in cases involving complex electron correlation effects. Despite DFT's effectiveness, the overlapping of peaks in the IR spectra necessitates additional analytical techniques, such as nuclear magnetic resonance (NMR) or Raman spectroscopy, to enhance the differentiation of isomers.

Keywords: Density Functional Theory, IR Spectra, Geometry Optimization

1 Introduction

In this study, author aim to advance the computational methodology established by Gurka and Titus applying Hartree-Fock (HF) by integrating Density Functional Theory (DFT) with a B3LYP functional [1].

DFT offers significant advantages over the conventional Hartree-Fock (HF) theory, particularly due to its capacity to consider electron correlation effects beyond the mean-field approximation. Mean-field electronic structure methods like Hartree–Fock, semilocal density functional approximations, or semiempirical molecular orbital (MO) theories do not account for long-range electron correlation (London dispersion interaction) [2]. Notably, a study conducted by Oleg Lukin and Jerzy Leszczynski in 2002 demonstrated the utility of the DFT method at the B3LYP/6-311(d,p) level in providing qualitative explanations for stability differences in investigated complexes compared to the ab initio HF method [3]. Patrick Huang and Emily A. Carter conducted a reviewed different techniques including the ubiquitous density functional theory (DFT) and its extensions such as DFT + U and hybrid DFT that locally refine the quantum treatment to improve accuracy[4]. Moreover, research by Ziegler in 1991 underscored the superiority of the DFT approach with the Hartree-Fock-Slater (HFS) method over ab initio HF method in describing molecular structure, as evidenced by lower mean absolute error[5]. Hence, DFT approximations can represent a refinement of the methodology employed by Gurka and Titus, who simulated nine isomers of Tetrachlorobutadiene (TCBD) at the HF level.

The research conducted by Gurka and Titus marks a significant contribution to the field of environmental chemistry, with a particular focus on the analysis of TCBDs, or chlorobutadienes. These compounds have garnered attention due to their potential environmental implications. In a study by Huang et al. (2014) investigating chlorinated organic compounds, it was revealed that these substances have prolonged environmental persistence, posing heightened health risks [6]. Furthermore, they contribute to ozone layer depletion, exacerbating health concerns for both humans and other organisms inhabiting the Earth. Annika Hanberg (1996) conducted research on various chlorinated organic compounds, highlighting their environmental persistence and carcinogenic properties. Particularly alarming was the finding that these compounds could be highly toxic to developing embryos, fetuses, and infants [7]. Gurka and Titus set out to explore the presence and characteristics of nine chlorinated butadiene compounds found in environmental samples. Employing a meticulous blend of experimental techniques such as gas chromatography/mass spectrometry (GC/MS) and Fourier transform infrared spectrometry (FT-IR), alongside computational modeling using ab initio Hartree-Fock (HF) theory, they aimed to shed light on the nature of these compounds. By leveraging HF theory, a foundational quantum mechanical approach, they were able to predict the vibrational frequencies and intensities of chlorobutadiene isomers, aiding in their identification and structural understanding. Through their combined experimental and computational approach, Gurka and Titus provided significant insights into the composition of environmental samples, enriching my understanding of chlorobutadiene contamination sources and pathways. Hartree-Fock (HF) theory has played a crucial role in the development of quantum chemistry, offering valuable insights into molecular structures, bonding, and electronic properties. However, despite its success, HF theory is limited by its treatment of electron correlation, which only accounts for mean-field interactions between electrons. This approximation becomes problematic in systems where strong electron correlation effects dominate, such as transition metal complexes, strongly correlated materials, and certain types of chemical reactions, leading to inaccurate predictions of molecular properties. To address these shortcomings, more advanced computational techniques have been developed that extend beyond the limitations of HF.

One of the most widely adopted methods is Density Functional Theory (DFT), which has emerged as a powerful alternative for the quantum mechanical computation of chemical properties. As noted by George Fitzgerald and Jan Andzelm, DFT offers a more sophisticated framework for calculating molecular properties by incorporating electron correlation effects through exchange-correlation functionals [8]. This makes DFT particularly well-suited for systems where HF theory falls short, as it provides a more accurate representation of the electron density and a more efficient computational strategy, especially for larger systems. Roberto Car and Michele Parrinello's groundbreaking work in DFT-based molecular dynamics further demonstrated the versatility of DFT in applications requiring large-scale electronic structure calculations and extensive sampling of molecular geometries, particularly in materials science and condensed matter physics [9]. Their work showed that DFT can handle both small molecules and complex materials, offering a balance between computational cost and accuracy that is difficult to achieve with post-HF methods like configuration interaction (CI) or coupled cluster theory (CC). More recently, advances in DFT have included the development of hybrid functionals, which combine aspects of HF theory with DFT to better account for electron exchange and correlation. Studies by Scuseria et al. [10] and the ongoing work in the field of meta-GGA functionals highlight how modern DFT approaches have narrowed the gap between computational efficiency and accuracy. These methods are increasingly being used to predict reaction mechanisms, transition states, and excited-state properties in ways that HF cannot match. Additionally, DFT has proven highly effective in the study of materials involving strong correlation effects, such as superconductors, magnetic materials, and high-pressure phases of matter, where HF-based approaches struggle. New developments in time-dependent DFT (TDDFT) and beyond-DFT methods, such as DFT+U or GW approximations, are providing even more accurate descriptions of complex systems, as highlighted in the recent review by Burke and coworkers [11]. These advancements have extended the applicability of DFT in quantum chemistry and condensed matter physics, pushing the boundaries of what can be computed with reasonable resources. Ultimately, while HF theory laid the foundation for computational quantum chemistry, its limitations necessitate the use of more sophisticated methods like DFT for a broader range of applications. The integration of DFT into modern computational chemistry continues to yield more reliable and precise insights, particularly in the study of complex systems characterized by strong electron correlation effects. As computational methods evolve, DFT's role will likely expand, incorporating new advancements in functional development and computational algorithms, further enhancing its accuracy and efficiency in predicting chemical properties.

According to a study by Nevin Oliphant and Rodney J. Bartlett, the relatively inexpensive hybrid Hartree–Fock density-functional-theory method yields results which represent a reliable, significant improvement over those obtained with the Hartree–Fock method [12]. Vincenzo Barone et. al. found that computational molecular spectroscopy, born as a branch of quantum chemistry to provide predictions of spectroscopic properties and features, emerged as an independent and highly specialized field and has progressively evolved to become a general tool [13]. By incorporating electron correlation, DFT enables a more precise characterization of molecular properties, rendering it well-suited for predicting vibrational frequencies and intensities of organic compounds. This study proposes the adoption of Density Functional Theory (DFT) coupled with a B3LYP functional, alongside other advanced functions from the Jacob's Ladder for the detection and analysis of chlorobutadiene compounds.

In this study, the primary aim is to enhance the computational analysis of Tetrachlorobutadiene (TCBD) isomers by incorporating Density Functional Theory (DFT) with the B3LYP functional. The research builds upon previous work, which primarily utilized the Hartree-Fock (HF) method, and seeks to overcome its limitations in accurately predicting molecular properties, particularly in systems with complex electron correlation effects. DFT, with its ability to include electron correlation beyond the mean-field approximation, provides a more robust and precise approach for molecular analysis. The study has several specific objectives. First, it aims to optimize the molecular geometries of nine different TCBD isomers, each with varying configurations of hydrogen and chlorine atoms, using advanced DFT methods. Second, the research seeks to compute the vibrational frequencies of these isomers and simulate their infrared (IR) spectra using the B3LYP and B3LYP-D3BJ functionals. These functionals are chosen due to their balance of computational efficiency and accuracy, particularly in capturing electron correlation and dispersion interactions. A key goal of the study is to compare the performance of DFT with the HF method in identifying functional groups and predicting the molecular structures of the TCBD isomers. By conducting a comparative analysis of the IR spectra generated by both methods, the study aims to demonstrate the superiority of DFT in terms of accuracy and consistency. This research ultimately seeks to provide a more reliable computational framework for analyzing chlorinated organic compounds like TCBD, which are of significant interest due to their environmental and chemical properties. Additionally, the study aims to validate the DFT-based computational model by comparing the simulated IR spectra with experimental data, ensuring the robustness of the findings.

2 Methodology

To differentiate molecules based on their structures, infrared (IR) spectroscopy can be utilized. For studying the nine isomers of Tetrachlorobutadiene (TCBD), the process involves several steps (Figure 1). Initially, the molecular structure is created. Following this, simulations are conducted to determine the stable geometry of each molecule. Once a stable configuration is achieved, IR intensity spectra are generated. Finally, the obtained data are compared with existing literature to evaluate the effectiveness of any modifications made during the process. This approach ensures accurate identification and analysis of the TCBD isomers through their IR spectra. First, the molecule was drawn using Molden software. After creating the structure, the 'Write Z-matrix' feature was employed to save a 'Gamess-US' coordinate output file with a '.com' extension. This Z-matrix was used as the input for Psi4 software to perform the geometry optimization step. The geometry optimization in Psi4 was carried out using Density Functional Theory (DFT) methods to determine the most stable molecular configurations, providing a robust foundation for further investigations. All the Z-matrices are presented in 'Appendix A. Z-matrices of the isomers', IR intensity data can be found in 'Appendix B. IR data from the simulation', and all the Python codes are available in 'Appendix C. Python codes' in the Supplementary Data file.

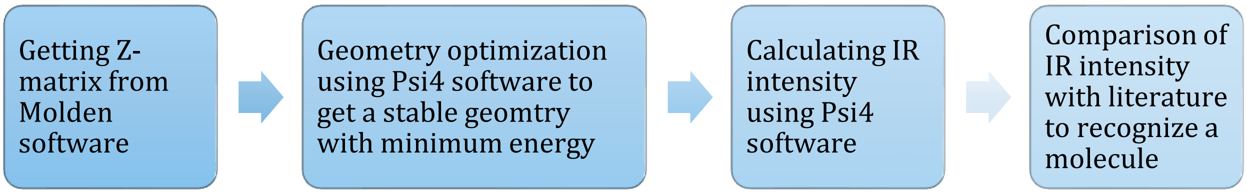


Figure 1: Block diagram of the methodology

Jacob's Ladder, a conceptual framework introduced by John P. Perdew in Density Functional Theory (DFT), serves as a guiding structure for developing and improving exchange-correlation functionals. This metaphorical ladder represents the progressive refinement of functionals, with each rung incorporating increasingly sophisticated physical effects, moving closer to the "heaven of chemical accuracy" in quantum chemistry calculations. Perdew's framework is essential for understanding how DFT functionals have evolved, balancing computational efficiency with accuracy, and has become a standard reference in the field of computational chemistry [14]. The first rung of Jacob's Ladder is the Local Density Approximation (LDA), which relies solely on local electron density to approximate exchange-correlation energy. LDA assumes that the electron density is uniform within small regions of space, which works reasonably well for simple systems like bulk metals or solids but struggles with molecular systems where electron density varies significantly [15]. Despite its limitations, LDA laid the foundation for DFT's widespread application, particularly in solid-state physics. However, its tendency to overestimate binding energies and underestimate band gaps in materials led to the development of more sophisticated methods.

The second rung, Generalized Gradient Approximation (GGA), builds on LDA by incorporating the gradient of the electron density, which accounts for non-homogeneous electron distributions. GGA functionals, such as the widely-used PBE (Perdew-Burke-Ernzerhof) functional, significantly improve accuracy for molecular systems and are commonly applied in chemical and materials science calculations [16]. By considering both the local density and its rate of change, GGA strikes a balance between simplicity and accuracy, making it one of the most popular choices for DFT calculations. However, GGA still has limitations in capturing long-range van der Waals interactions and strong correlation effects. The third rung of Jacob's Ladder, Meta-GGA, takes another step forward by including second-order density derivatives, such as the kinetic energy density. Meta-GGA functionals, like the TPSS functional (Tao-Perdew-

Staroverov-Scuseria), aim to improve upon GGA by incorporating even more detailed information about the electron density distribution [17]. Meta-GGA functionals have shown promise in capturing intermediate correlation effects and predicting more accurate thermodynamic properties, reaction barriers, and non-covalent interactions compared to GGA. This rung provides a useful trade-off between computational cost and accuracy, especially for organic molecules, transition states, and catalysis.

The fourth rung of Jacob's Ladder introduces hybrid functionals, which blend a portion of the exact exchange energy from Hartree-Fock theory with DFT calculations. Hybrid functionals, such as B3LYP (Becke, three-parameter, Lee-Yang-Parr), are widely regarded for their accuracy in predicting molecular geometries, bond energies, and vibrational frequencies [18]. By incorporating a fraction of exact exchange, hybrid functionals correct for some of the deficiencies of pure DFT functionals, such as delocalization errors and underestimation of excitation energies. Hybrid methods are extensively used in quantum chemistry for both organic and inorganic systems, although their computational cost is higher than GGA and Meta-GGA functionals. At the top of the ladder lies the fifth rung: Double-Hybrid Functionals. These functionals incorporate not only Hartree-Fock exchange but also perturbative correlation energy from methods like second-order Møller-Plesset perturbation theory (MP2) [19]. Double-hybrid functionals, such as B2PLYP, offer the highest level of accuracy among commonly used DFT methods, particularly for thermochemistry and reaction energetics. However, their increased computational cost limits their application to smaller systems. Despite this, double-hybrids represent the pinnacle of Jacob's Ladder, providing unprecedented accuracy for complex systems, especially those with significant electron correlation effects, such as excited states or transition metals.

This hierarchical framework of Jacob's Ladder is invaluable for researchers as it provides a clear guide for selecting the appropriate functional based on the trade-off between computational cost and accuracy. For systems where computational resources are limited or where approximate results are sufficient, functionals from the lower rungs, such as GGA or Meta-GGA, are suitable. However, when high accuracy is paramount, as in reaction energy calculations or electronic structure predictions for complex systems, higher-rung functionals like hybrids or double-hybrids are preferred. In recent years, there has been significant progress in refining functionals at each rung of the ladder. Newer hybrid and meta-GGA functionals, such as SCAN (Strongly Constrained and Appropriately Normed), have shown promise in improving the accuracy of DFT calculations for a wide range of systems, from small organic molecules to complex materials [20]. These advancements are pushing the boundaries of what DFT can achieve, narrowing the gap between computational and experimental results, and further solidifying the importance of Jacob's Ladder as a guiding principle in the evolution of DFT (Figure 2).

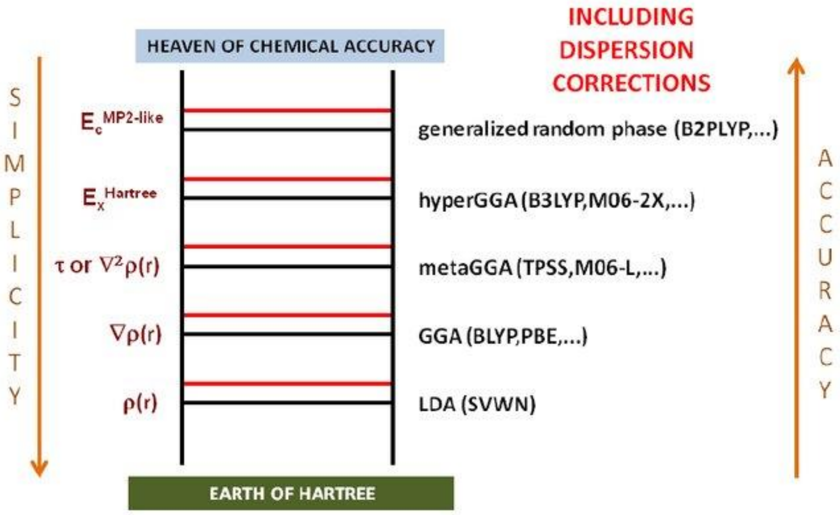


Figure 2: *Jacob's ladder approach for the systematic improvement of DFT functionals according to the metaphor of Perdew and Schmidt[21] showing some of the most common functionals within each rung [22].*

For this study, Density Functional Theory (DFT) was employed using the B3LYP functional and the 6-31G* basis set to compute both the initial geometry optimization and vibrational frequencies of six isomers from a total of nine isomers. The B3LYP functional is a widely used hybrid functional in computational chemistry and belongs to the fourth rung of Perdew's Jacob's Ladder framework in DFT. Hybrid functionals, such as B3LYP, offer a balanced approach by incorporating exact exchange from Hartree-Fock (HF) theory into the Generalized Gradient Approximation (GGA) or Meta-GGA framework, thereby improving the accuracy of DFT calculations, especially for systems with moderate electron correlation effects. The selection of B3LYP for this study was motivated by its ability to handle larger molecular systems without imposing excessive computational demands, while still providing a reasonable level of accuracy in predicting molecular properties.

For the remaining three isomers, the B3LYP-D3BJ functional combined with the cc-pVDZ basis set was utilized. B3LYP-D3BJ is a variant of the B3LYP functional that includes Grimme's D3 dispersion correction with Becke-Johnson (BJ) damping, making it more suitable for capturing non-covalent interactions such as van der Waals forces. This method is particularly effective for systems where dispersion interactions play a significant role in the stabilization of molecular geometries. The vibrational frequencies and infrared (IR) intensities for these isomers were calculated based on the optimized geometries using the Psi4 software package, a robust quantum chemistry software designed for ab initio calculations, including DFT. The DFT calculations, performed at the optimized geometries, enabled accurate predictions of the IR spectra for each isomer. The vibrational frequencies of molecules are directly related to the motion of atoms within the chemical bonds. These characteristic vibrational frequencies manifest in the infrared (IR) spectrum, making IR spectroscopy a powerful tool for identifying functional groups and understanding molecular structures. By simulating the IR spectra of the isomers, the study could identify specific functional groups within each isomer, providing insights into their molecular structures. The simulated IR spectra also enabled the comparison of vibrational modes across different isomers, facilitating a deeper understanding of their structural differences.

In the final stage of the study, a comparative analysis was conducted on the IR spectra of the nine isomers of chlorobutadiene compounds (TCBD isomers). This comparison was crucial for elucidating their molecular structures and provided a systematic way to distinguish between different isomers based on their vibrational signatures. Additionally, the DFT-simulated IR spectra were compared with IR spectra generated using the Hartree-Fock (HF) method to assess the relative accuracy of DFT versus HF in predicting vibrational frequencies and IR intensities. To further validate the computational results, the simulated IR spectra were compared against experimental IR data. This validation step ensured the reliability and robustness of the computational model employed in the study. The ability of DFT, particularly the B3LYP and B3LYP-D3BJ functionals, to accurately simulate the IR spectra and predict the vibrational properties of the TCBD isomers demonstrated the method's effectiveness in elucidating molecular structures. The comparative analysis between the DFT-based simulations and experimental IR spectra also provided rigorous validation for the DFT model, solidifying its credibility in studying the molecular structures of complex systems like TCBD compounds. Ultimately, the study's findings underscore the utility of hybrid DFT functionals like B3LYP and dispersion-corrected functionals like B3LYP-D3BJ in predicting molecular geometries and vibrational spectra with a high degree of accuracy. This methodological approach allowed for a comprehensive and detailed understanding of the structural properties of the TCBD isomers, thereby contributing to the broader field of computational chemistry and molecular spectroscopy.

3 Results and Discussions

3.1 Structure of the Isomers drawn in Molden

TCBD (Tetrachlorobutadiene) consists of a total of four carbon atoms, two hydrogen atoms, and four chlorine atoms. In their research, Gurka and Titas examined nine distinct isomers of TCBD, each characterized by different placements of hydrogen and chlorine atoms within the molecule. The molecular structures of these isomers are illustrated in Figure 3, which presents the specific arrangements of the atoms. To offer a clearer and more intuitive view of the molecular geometries, Figure 4 provides ball-and-stick models of the TCBD isomers, which were created using the Molden/6.2 visualization software. The Z-matrix representations of these isomers, detailing their precise atomic coordinates, are available in the supplementary data file section titled "Additional Data." In addition to the structural representations, Figure 5 highlights the infrared (IR) spectra of the nine TCBD isomers, computed using Density Functional Theory (DFT) with the B3LYP and B3LYP-D3BJ functionals. A particular focus is given to isomer a, identified as the (E,E)-1,2,3,4-TCBD isomer, which is located in the top-left corner of the IR plot. Several key IR features are observed for this isomer. A significant peak is detected around 801 cm^{-1}, representing the C-Cl stretching motion, a characteristic vibration of chlorobutadienes [23]. Additionally, a medium-intensity peak at 832 cm^{-1} corresponds to the C=C bending mode, a fundamental vibration in chlorobutadiene compounds. Further notable peaks include a medium-intensity signal at 860 cm^{-1}, indicative of the C-H bending motion. Moving to higher wavenumbers, a medium peak at 1586 cm^{-1} represents the C=C stretching vibrations, which are commonly observed in alkenes. Lastly, at 3252 cm^{-1}, a medium-intensity peak is visible, signaling the C-H stretching motion in the alkene moiety of the molecule. This comprehensive vibrational analysis provides detailed insights into the structural and bonding characteristics of the TCBD isomers, with each peak in the IR spectrum corresponding to specific molecular vibrations. The corresponding numerical data for the IR intensities and wavenumbers are available in the "Additional Data" section, offering further reference for detailed examination. Through the use of DFT methods, particularly B3LYP and B3LYP-D3BJ, the researchers were able to accurately model the molecular vibrations of the TCBD isomers, thus enhancing the understanding of their chemical structures and interactions.

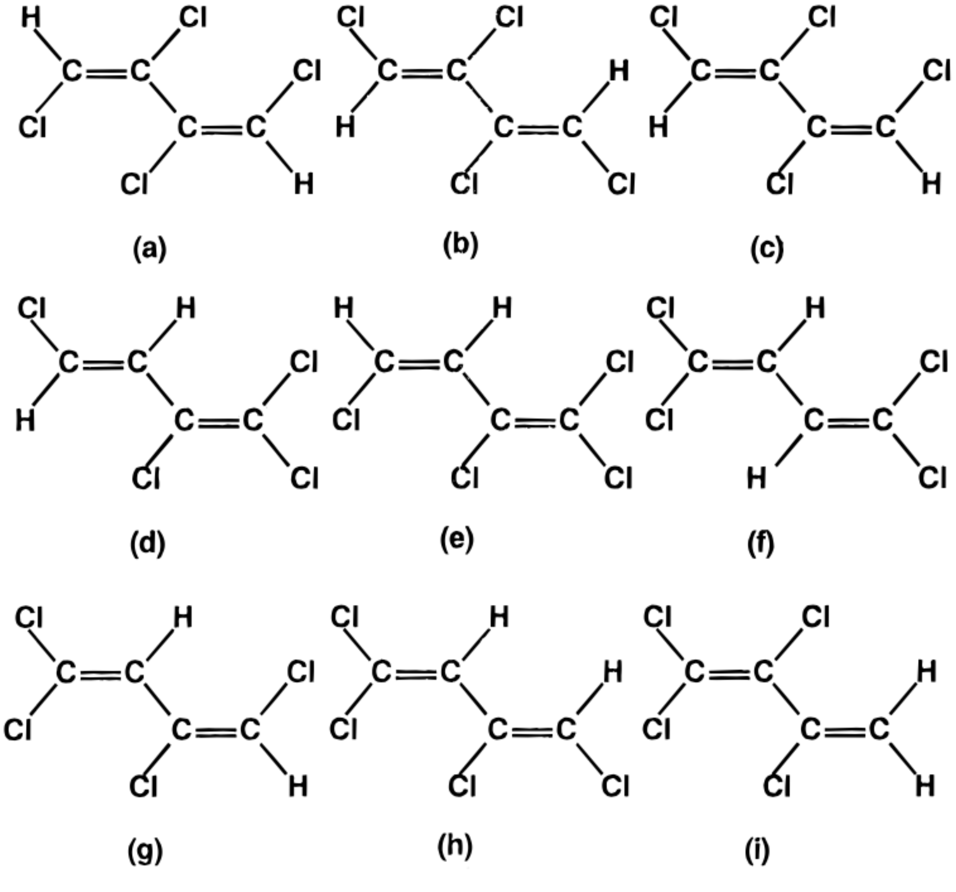
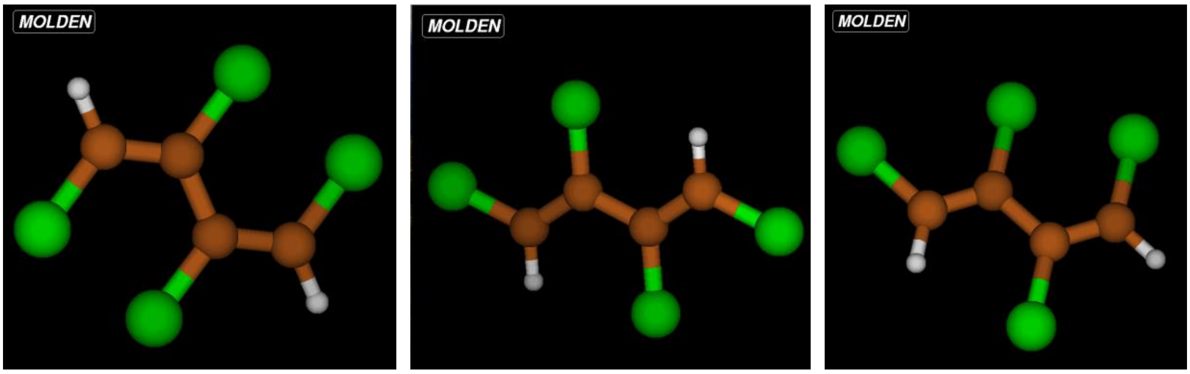
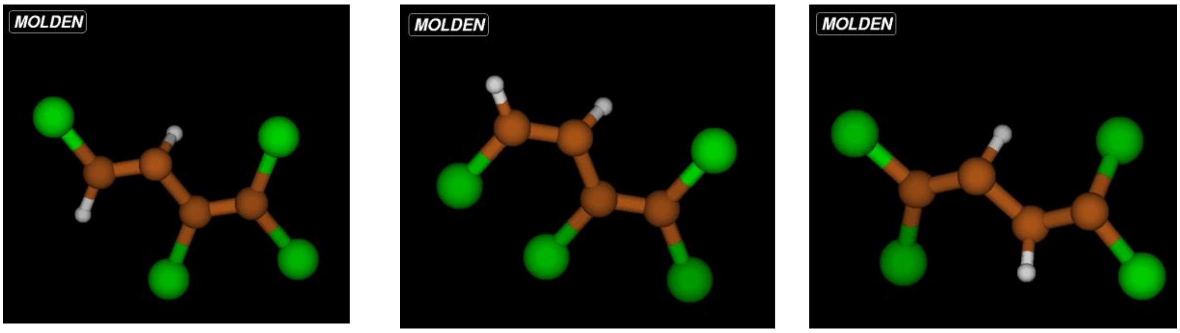


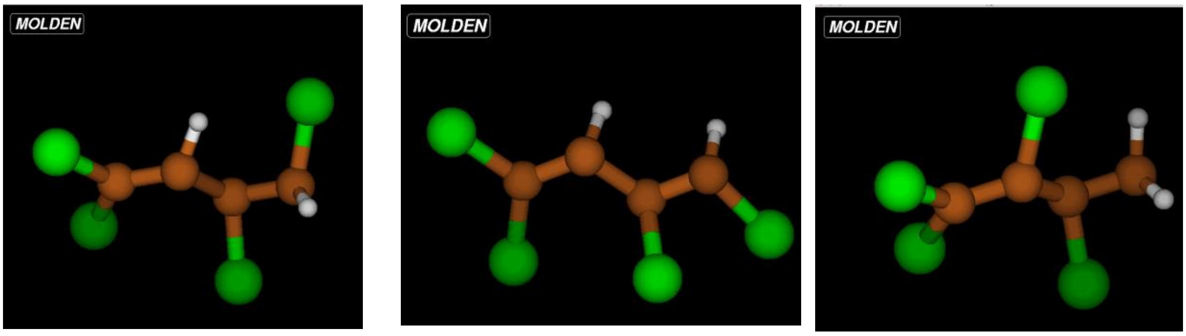
Figure 3: *Molecular structure of nine isomers of Tetrachlorobutadiene (TCBD)[1]*



(a) (E,E)-1,2,3,4-TCBD (b) (Z,Z)-1,2,3,4-TCBD (c) (E,Z)-1,2,3,4-TCBD



(d) (Z)-1,1,2,4-TCBD (e) (Z,Z)-1,2,3,4-TCBD (f) 1,1,4,4-TCBD



(g) (E)-1,1,3,4-TCBD (h) (Z)-1,1,3,4-TCBD (i) 1,1,2,3-TCBD

Figure 4: *Molecular structure for nine isomers of Tetrachlorobutadiene (TCBD). The brown ball is carbon atom, the silver ball is hydrogen atom, and the green ball is chlorine atom.*

3.2 IR spectroscopy using DFT method

Similar peaks were observed for molecule B, suggesting its classification as an alkene due to the presence of characteristic C=C stretching vibrations. In addition to this, the bending of the halo compound's C-Cl bond was detected, alongside the bending and stretching of the C-H bond. These vibrational modes, which indicate both halogen and hydrocarbon bond motions, were consistent across the remaining TCBD isomers, ranging from TCBDc to TCBDi. The recurrence of these patterns reinforces the similarity in molecular structure among the isomers, particularly with regard to their alkene characteristics and halogen interactions. A detailed breakdown of the infrared (IR) spectroscopy absorptions for these isomers, arranged by specific frequency regions, is provided in Table 1. This table organizes the observed peaks and correlates them with their respective vibrational modes, offering a comprehensive view of the molecular dynamics in the TCBD isomers. The absorption regions cover a range of motions including stretching and bending vibrations of C=C, C-H, and C-Cl bonds, highlighting key features of alkene and halogen-containing molecules. Table 2 complements this analysis by presenting the IR spectra values generated through Density Functional Theory (DFT) for each of the observed peaks. These values are categorized based on their relative strength, with peaks classified as strong (s), medium (m), or weak (w), depending on their intensity. The strongest peaks are associated with the maximum absorption values, which typically signify the most prominent vibrational modes in the molecular structure. This categorization allows for an easier comparison of vibrational intensities across different isomers, providing insights into the relative significance of various bond motions within each molecule. The detailed data from Tables 1 and 2 offer a valuable resource for interpreting the IR spectra and understanding the molecular structures of the TCBD isomers.

Table 1: *Corresponding IR spectra Absorption values from the literature for the peaks found in the TCBD isomers.[23]*

Frequency (cm^{-1})	**Relative strength**	**Shape of peak**	**Bond**	**Vibrational Mode**	**Group**	**Type of bond/molecule**
3100-3000	medium	-	C-H	stretching	alkene	-
1648-1638	strong	-	C=C	stretching	alkene	monosubstituted
880 ± 20 810 ± 20	strong	-	C-H	bending	1,2,4-trisubstituted	-
840-790	medium	-	C=C	bending	alkene	trisubstituted
780 ± 20 (700 ± 20)	strong	-	C-H	bending	1,2,3-trisubstituted	-

The analysis of Figure 3, Figure 4, Figure 5, Table 1, and Table 2 collectively highlights the effectiveness of Density Functional Theory (DFT) in accurately identifying the various isomers of TCBD using different hierarchical functionals. DFT proves capable of predicting molecular geometries and vibrational modes across the isomers, showcasing its utility in computational chemistry. However, distinguishing between the isomers solely based on their infrared (IR) spectra presents challenges, as many of the vibrational peaks overlap or are too similar to provide clear differentiation. This indicates the limitations of relying exclusively on IR spectroscopy for distinguishing structural variations among isomers. Consequently, alternative analytical techniques—such as nuclear magnetic resonance (NMR) spectroscopy, Raman spectroscopy, or advanced computational methods—are needed to enhance the resolution and provide a more comprehensive identification of TCBD isomers. Combining multiple approaches may lead to more accurate and reliable molecular characterization.

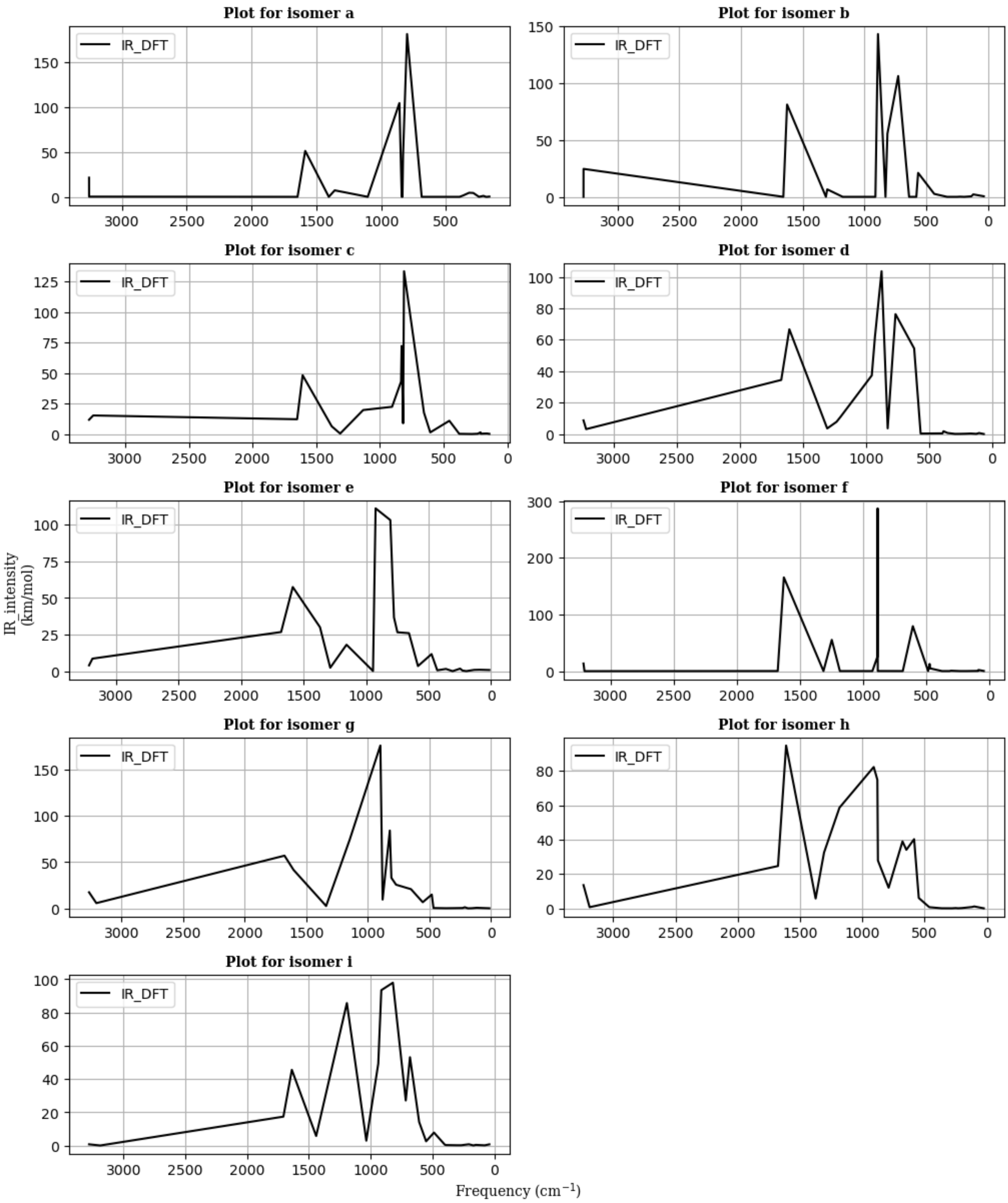


Figure 5: *Infrared (IR) spectra for nine isomers of tetrachlorobutadiene (TCBD) using DFT method*

3.3 Comparison of IR spectroscopy between DFT method and HF method

Figure 6 presents a detailed comparison of the infrared (IR) spectra obtained using both Density Functional Theory (DFT) and Hartree-Fock (HF) methods for isomers a, b, and c, as derived from the data in Table 2 of the study by Gurka and Titus. Upon close examination, a significant difference in the effectiveness of these two computational approaches becomes apparent. The IR spectra generated by the DFT method show a higher number of distinct peaks, corresponding to various functional groups within the TCBD molecule, in stark contrast to the relatively sparse peaks in the HF-derived spectra. This difference is particularly notable because the HF method is expected to produce reliable spectra for small molecules, yet the similar shapes of the DFT spectra indicate its superior performance. In contrast, the HF spectra, despite the structural similarities of the isomers, show more variation, a surprising result that underscores the limitations of the HF method. Notably, only isomer c could be accurately characterized using HF, except for the C-H stretch, which should exhibit a medium-intensity peak around 3100-3000 cm^{-1}. This observation further emphasizes that DFT outperforms HF in its ability to provide a detailed and accurate depiction of molecular structures, particularly when identifying the functional groups within complex molecules like TCBD.

In Figure 7, the IR spectra for isomers d, e, and f are illustrated, showcasing additional disparities between the HF and DFT methods. Specifically, the HF method failed to detect all functional groups in isomers d and f, missing key vibrational modes. For isomer e, HF managed to identify several vibrational frequencies, though it notably failed to capture the C-H stretch. In contrast, DFT, particularly when using the more advanced B3LYP-D3BJ functional and cc-pVDZ basis set, succeeded in identifying all the relevant functional groups and vibrational modes across these isomers. This not only highlights the adaptability and precision of the DFT approach but also underscores its comprehensive capability in detecting molecular properties with a higher degree of accuracy than HF. The improved performance of DFT, especially with the inclusion of dispersion corrections, makes it a more reliable method for complex molecular systems where the HF method may fall short. Figure 8 focuses on the IR spectra of isomers g, h, and i, and offers an interesting contrast to earlier observations. In these cases, the HF method provided a more thorough analysis compared to its performance with earlier isomers, with several additional peaks detected at the expected frequencies. This improved performance, while notable, still fell short of capturing the C-H stretch, once again reflecting the method's limitations. On the other hand, the DFT method, using the B3LYP functional, successfully identified all the relevant vibrational modes and functional groups across these isomers. This consistent accuracy, particularly with regard to detecting the C-H and C-Cl stretching vibrations, reinforces the superiority of the DFT method in identifying molecular properties, even in cases where HF demonstrates some degree of success. The use of the B3LYP functional, which combines Hartree-Fock exchange with DFT, ensures a more precise calculation of electron interactions and molecular vibrations, making it the preferred method for studying the TCBD molecule.

Table 2: *IR spectra for the TCBD isomers using DFT methods*

Frequency (cm^{-1})	**IR Intensity (km/mol)**	**Relative intensity***	**Frequency (cm^{-1})**	**IR Intensity (km/mol)**	**Relative intensity**	**Frequency (cm^{-1})**	**IR Intensity (km/mol)**	**Relative intensity**
Isomer a**			**Isomer d*****			**Isomer g****		
801	181	s	618	54	m	648	21	w
832	47	m	766	76	m-s	770	26	w
860	104	m-s	828	4	w	808	33	w
1358	7	w	876	104	s	820	84	m
1586	51	m	929	62	m	879	9	w
3252	21	m	954	37	m	897	176	s
Isomer b**			1198	11	w	1146	75	m
727	106	s	1233	8	w	1338	3	w
814	55	m	1307	4	w	1360	6	w
891	143	s	1607	67	m	1603	42	w-m

1302	7	w	1671	34	m	1677	57	w-m
1627	81	m-s	3218	3	w	3206	6	w
3275	25	w-m	3239	9	w	3265	17	w
Isomer c**			**Isomer e*****			**Isomer h****		
654	17	w	657	26	m	646	34	w-m
810	133	s	749	27	m	677	39	w-m
818	9	w	777	37	m	789	12	w
829	72	m	806	103	s	875	28	w-m
834	43	m	924	111	s	879	75	s
904	22	w	1157	18	w-m	908	82	s
1131	20	w	1287	2	w	1183	59	m
1378	6	w	1369	30	m	1307	33	w-m
1607	48	m	1587	58	m	1375	6	w
1650	12	w	1680	27	m	1611	95	s
3252	15	w	3190	9	w	1677	25	w
3285	12	w	3218	4	w	3189	1	w
						3238	14	w
			f***			**i****		
			608	80	m	607	14	w
			887	287	s	681	53	m
			889	26	w	715	27	w-m
			1249	55	w-m	820	98	s
			1629	165	s	913	93	s
			3214	14	w	938	49	m
						1035	3	w
						1192	86	s
						1441	6	w
						1638	46	m
						1706	17	w
						3279	1	w

* = Relative to the strongest intensity

** = Method (B3LYP/6-31G*)

*** = Method (B3LYP-D3BJ/cc-pVDZ)

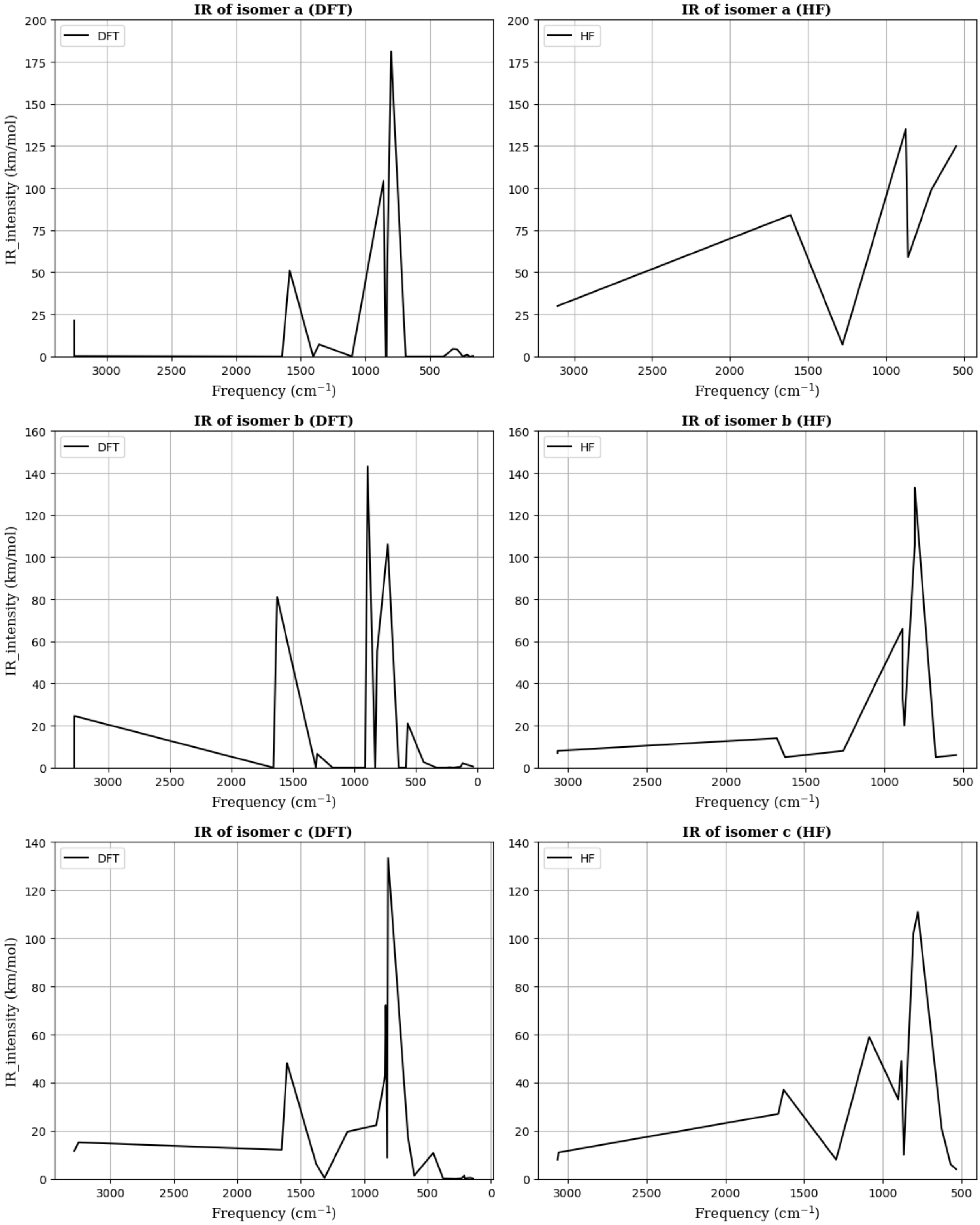


Figure 6: *IR Spectra for isomers a, b, and c in DFT and HF method*

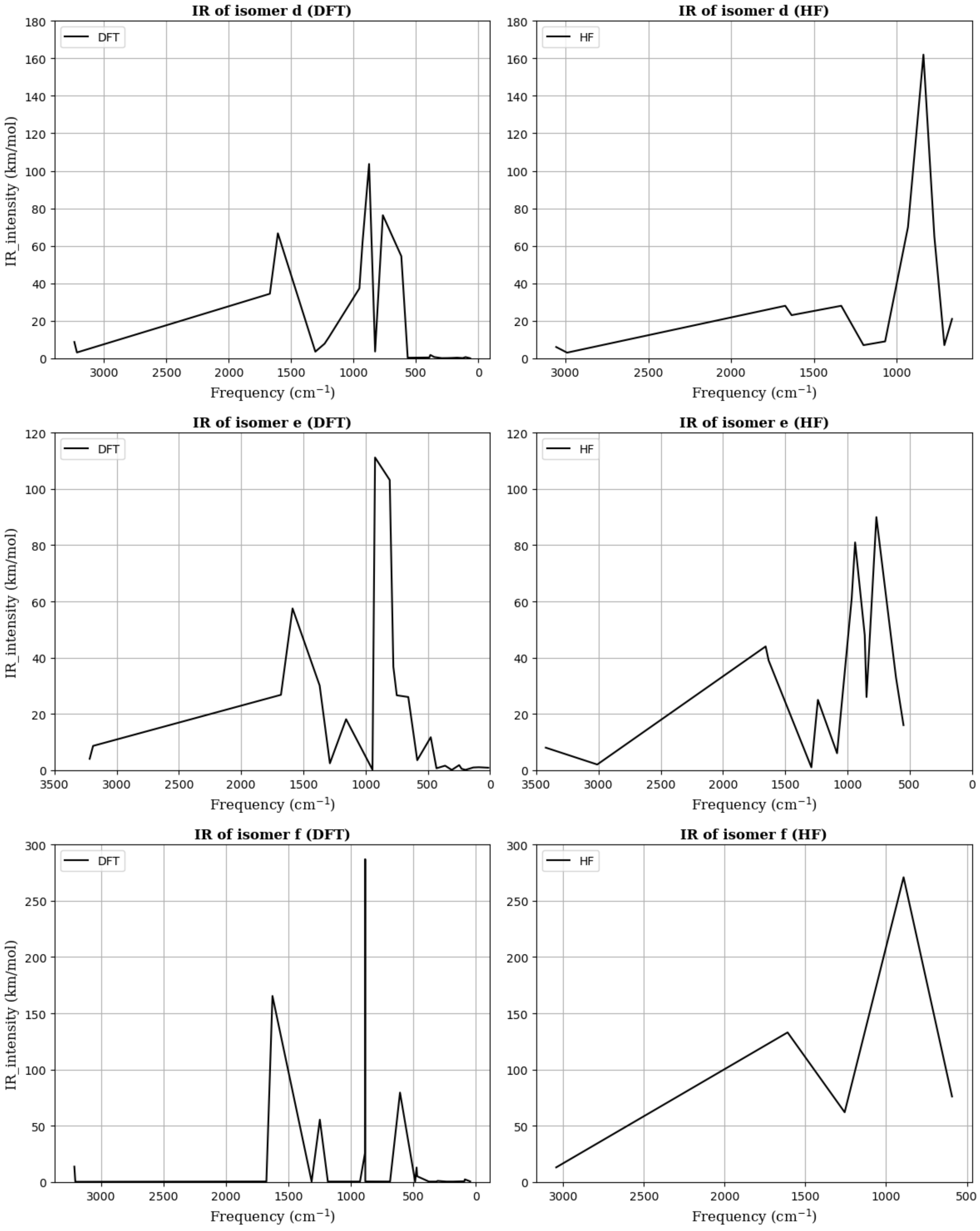


Figure 7: *IR Spectra for isomer TCBD d, e, and f in DFT and HF method*

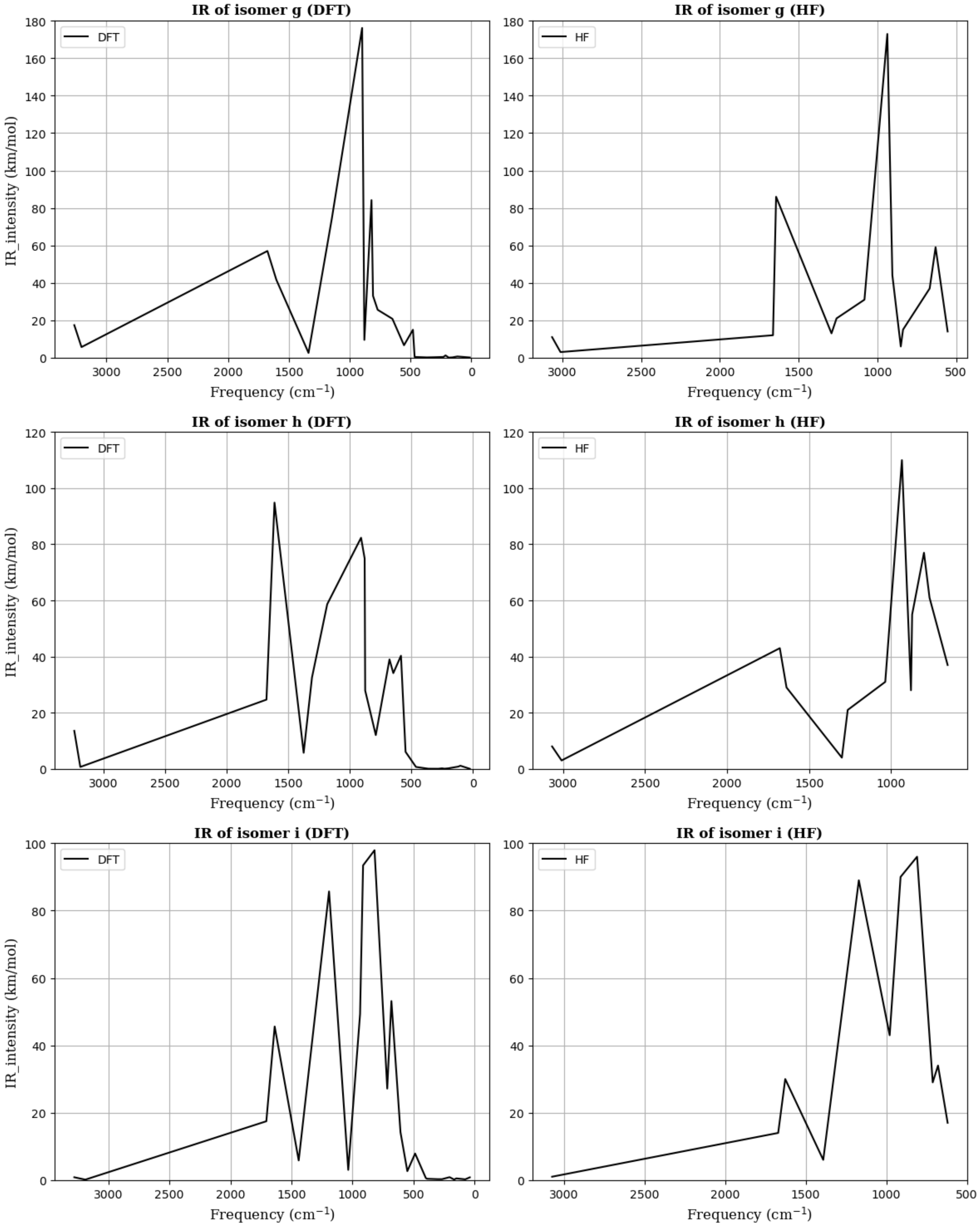


Figure 8: *IR Spectra for isomer TCBD g, h, and i in DFT and HF method*

4 Conclusion

The study concludes that Density Functional Theory (DFT) is significantly more effective than the Hartree-Fock (HF) method in identifying and analyzing the molecular structures and functional groups of TCBD isomers. DFT's ability to account for electron correlation effects and generate more distinct and consistent peaks across isomers underscores its superiority. While HF struggles to detect certain functional groups, DFT accurately identifies the vibrational frequencies of all relevant bonds, particularly C-H and C-Cl stretches. The results align with existing literature, further validating the robustness of DFT as a computational tool for studying complex molecular systems. However, the overlapping of IR peaks indicates that future research could benefit from incorporating other techniques, such as NMR or Raman spectroscopy, to fully differentiate between isomers. Ultimately, the findings emphasize the importance of using advanced DFT methods for accurate molecular characterization in environmental chemistry and beyond.

5 Declarations

5.1 Acknowledgement

I gratefully acknowledge the invaluable support and resources provided by the SeaWulf computational cluster at Stony Brook University. Additionally, I extend my sincere appreciation to Professor Benjamin Levine of the Department of Chemistry at SUNY Stony Brook, New York. Professor Levine's guidance, expertise, and unwavering support have been instrumental throughout this study.

5.2 Competing Interests

The authors declared that no conflicts of interest exist in this work.

5.3 Publisher's Note

How to Cite this Article:

K. Fatema, "Detection of Tetrachlorobutadiene Isomers Using Density Functional Theory Methods: A Comparative Study of Hartree-Fock and Density Functional Theory Analysis", *J. Mod. Sim. Mater.*, vol. 7, no. 1, pp. 1–17, Feb. 2025. https://doi.org/10.21467/jmsm.7.1.1-17

Supplementary File

Supplementary data file is available at URL https://journals.aijr.org/index.php/jmsm/article/view/9523/608

References

[1] D. F. Gurka *et al.*, "Environmental Analysis by ab Initio Quantum Mechanical Computation and Gas Chromatography/Fourier Transform Infrared Spectrometry," *Anal. Chem.*, vol. 68, no. 23, pp. 4221–4227, Dec. 1996, doi: 10.1021/ac960463g.

[2] S. Grimme, A. Hansen, J. G. Brandenburg, and C. Bannwarth, "Dispersion-Corrected Mean-Field Electronic Structure Methods," *Chem. Rev.*, vol. 116, no. 9, pp. 5105–5154, May 2016, doi: 10.1021/acs.chemrev.5b00533.

[3] O. Lukin and J. Leszczynski, "Rationalizing the Strength of Hydrogen-Bonded Complexes. Ab Initio HF and DFT Studies," *J. Phys. Chem. A*, vol. 106, no. 29, pp. 6775–6782, Jul. 2002, doi: 10.1021/jp0145154.

[4] P. Huang and E. A. Carter, "Advances in Correlated Electronic Structure Methods for Solids, Surfaces, and Nanostructures," *Annu. Rev. Phys. Chem.*, vol. 59, no. Volume 59, 2008, pp. 261–290, May 2008, doi: 10.1146/annurev.physchem.59.032607.093528.

[5] Tom. Ziegler, "Approximate density functional theory as a practical tool in molecular energetics and dynamics," *Chem. Rev.*, vol. 91, no. 5, pp. 651–667, Jul. 1991, doi: 10.1021/cr00005a001.

[6] B. Huang, C. Lei, C. Wei, and G. Zeng, "Chlorinated volatile organic compounds (Cl-VOCs) in environment — sources, potential human health impacts, and current remediation technologies," *Environ. Int.*, vol. 71, pp. 118–138, Oct. 2014, doi: 10.1016/j.envint.2014.06.013.

[7] A. Hanberg, "Toxicology of Environmentally Persistent Chlorinated Organic Compounds," *Pure Appl. Chem.*, vol. 68, no. 9, pp. 1791–1799, Sep. 1996, doi: 10.1351/pac199668091791.

[8] J. K. Labanowski and J. W. Andzelm, *Density Functional Methods in Chemistry*. Springer Science & Business Media, 2012.

[9] R. Car and M. Parrinello, "Unified Approach for Molecular Dynamics and Density-Functional Theory," *Phys. Rev. Lett.*, vol. 55, no. 22, pp. 2471–2474, Nov. 1985, doi: 10.1103/PhysRevLett.55.2471.

[10] A. J. Garza, O. I. Osman, A. M. Asiri, and G. E. Scuseria, "Can Gap Tuning Schemes of Long-Range Corrected Hybrid Functionals Improve the Description of Hyperpolarizabilities?," *J. Phys. Chem. B*, vol. 119, no. 3, pp. 1202–1212, Jan. 2015, doi: 10.1021/jp507226v.

[11] K. Burke, "Perspective on density functional theory," *J. Chem. Phys.*, vol. 136, no. 15, p. 150901, Apr. 2012, doi: 10.1063/1.4704546.

[12] N. Oliphant and R. J. Bartlett, “A systematic comparison of molecular properties obtained using Hartree–Fock, a hybrid Hartree–Fock density-functional-theory, and coupled-cluster methods,” *J. Chem. Phys.*, vol. 100, no. 9, pp. 6550–6561, May 1994, doi: 10.1063/1.467064.

[13] V. Barone *et al.*, “Computational molecular spectroscopy,” *Nat. Rev. Methods Primer*, vol. 1, no. 1, pp. 1–27, May 2021, doi: 10.1038/s43586-021-00034-1.

[14] J. P. Perdew and K. Schmidt, “Jacob’s ladder of density functional approximations for the exchange-correlation energy,” *AIP Conf. Proc.*, vol. 577, no. 1, pp. 1–20, Jul. 2001, doi: 10.1063/1.1390175.

[15] W. Kohn and L. J. Sham, “Self-Consistent Equations Including Exchange and Correlation Effects,” *Phys. Rev.*, vol. 140, no. 4A, pp. A1133–A1138, Nov. 1965, doi: 10.1103/PhysRev.140.A1133.

[16] J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized Gradient Approximation Made Simple,” *Phys. Rev. Lett.*, vol. 77, no. 18, pp. 3865–3868, Oct. 1996, doi: 10.1103/PhysRevLett.77.3865.

[17] J. P. Perdew, “Climbing the ladder of density functional approximations,” *MRS Bull.*, vol. 38, no. 9, pp. 743–750, Sep. 2013, doi: 10.1557/mrs.2013.178.

[18] K. Raghavachari, “Perspective on ‘Density functional thermochemistry. III. The role of exact exchange,’” *Theor. Chem. Acc.*, vol. 103, no. 3, pp. 361–363, Feb. 2000, doi: 10.1007/s002149900065.

[19] S. Grimme, “Semiempirical GGA-type density functional constructed with a long-range dispersion correction,” *J. Comput. Chem.*, vol. 27, no. 15, pp. 1787–1799, 2006, doi: 10.1002/jcc.20495.

[20] J. Sun, A. Ruzsinszky, and J. P. Perdew, “Strongly Constrained and Appropriately Normed Semilocal Density Functional,” *Phys. Rev. Lett.*, vol. 115, no. 3, p. 036402, Jul. 2015, doi: 10.1103/PhysRevLett.115.036402.

[21] J. P. Perdew and K. Schmidt, “Jacob’s ladder of density functional approximations for the exchange-correlation energy,” *AIP Conf. Proc.*, vol. 577, no. 1, pp. 1–20, Jul. 2001, doi: 10.1063/1.1390175.

[22] J. Gomes *et al.*, “Density functional treatment of interactions and chemical reactions at surfaces,” in *Density Functional Theory: Principles, Applications and Analysis*, 2013, p. Density functional treatment of interactions and chemical reactions at surfaces.

[23] “Infrared Spectroscopy Absorption Table,” Chemistry LibreTexts. Accessed: May 04, 2024. [Online]. Available: https://chem.libretexts.org/Ancillary_Materials/Reference/Reference_Tables/Spectroscopic_Reference_Tables/Infrared_Spectroscopy_Absorption_Table