Molecular Structure, Vibrational Analysis, Molecular Electrostatic Potential and HOMO-LUMO Analysis of 2, 3, 3, 3-Tetrafluoropropene (HFO-1234yf)-An Environment Friendly Refrigerant

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Abstract: *The present study employs the DFT approach to perform a theoretical structural analysis of 2,3,3,3-Tetrafluoropropene (HFO-1234yf), which leads to the characterization of its molecular structure, harmonic vibrational frequencies, molecular properties, molecular electrostatic potential (MEP) mapping, and HOMO-LUMO analysis. The calculated geometrical parameters and frequencies of the fundamentals are determined to exhibit a satisfactory level of agreement with the experimental data.*

Keywords: DFT, Optimized geometry, Vibrational frequencies

1. Introduction

The depletion of the ozone layer poses a significant threat to human health and the environment. Increased levels of UV radiation reaching the Earth's surface can result in non-melanoma skin cancer and contribute to the development of malignant melanoma. Additionally, UV radiation can alter the physiological and developmental processes of plants, leading to changes in plant form, nutrient distribution, and ultimately, important ecological implications related to plant such as competitive balance, herbivory, plant diseases, and biogeochemical cycles. Disruption of the natural equilibrium between stratospheric ozone production and destruction leads to ozone depletion. Although natural phenomena can also contribute to this phenomenon, the emission of CFCs from anthropogenic activities is now considered a major cause of ozone depletion [1]. Ozone-depleting substances invariably contain chlorine and bromine [2]. Chlorofluorocarbons (CFCs) possess high volatility and low combustibility, allowing them to swiftly evaporate and infiltrate the stratosphere where they initiate ozone depletion. It is widely accepted that the forthcoming generation of refrigerants must be free of ozone depletion potential and exhibit low global warming potential. Various countries have proposed regulations enforcing the adoption of refrigerants with reduced environmental impact and improved energy efficiency, in agreement with this consensus. Due to the harmful environmental consequences of releasing chlorofluorocarbons (CFCs) into the atmosphere, a worldwide effort has been launched to substitute these compounds with environmentally suitable alternatives. Unsaturated fluorinated hydrocarbons have been developed as a replacement for CFCs and hydrofluorocarbons (HCFCs) in air conditioning systems. This drive was primarily prompted by the ozone-depleting potential of CFCs and HCFCs, which were commonly used in refrigeration and led to the phase-out of CFC12. Research is currently underway to create novel fluids with low global warming potential to support the refrigeration and air conditioning sector, such as 2,3,3,3-Tetrafluoropropene (HFO-1234yf) [3].Zilio et al. [4] conducted research on a small European car in 2009, and found no significant decline in the cooling capacity and coefficient of performance (COP) of HFO-1234yf in comparison to HFC-134a. With a 100-year global warming potential (GWP) of 4, HFO-1234yf can be used as a "near drop-in replacement" for HFC-134a, without necessitating major modifications to assembly lines or vehicle system designs. The thermophysical properties of HFO-1234yf are similar to those of HFC-134a, making significant equipment changes unnecessary. The refrigerant displays desirable environmental properties, such as an ozone depletion potential (ODP) of 0, a GWP of 4, an atmospheric lifetime (ALT) of 11 days, and appropriate lower carbon footprint (LCCP) [5]. Brown et al. [6] studied the replacement of R114 with HFO-1234yf and found that HFO-1234yf exhibited a higher volumetric heat capacity and COP. Recently, Zhang et al. [7] theoretically investigated non-azeotropic mixtures of HFOs, including HFO-1234yf, as replacements for HFC-134a and CFC-114 in heat pumps. Their findings indicate that certain compositions of these mixtures can yield proper COP and may be a superior replacement for HCFC-134a and CFC-114. Mathur et al. [8] conducted experimental research to determine the air conditioning (A/C) performance using HFO-1234yf as a drop-in alternative to HFC-134a. Their results demonstrated that the refrigerant mass charge for HFO-1234yf was 90% lower than that of HFC-134a, while also exhibiting superior cooling capacity, COP, and lower working pressure of the parallel flow condenser.

Lee and Jung [9] conducted an assessment of HFO-1234yf as a drop-in replacement for HFC-134a in mobile air conditioners using a heat pump testing bench. The tests showed that the COP of HFO-1234yf was slightly lower than that of HFC-134a by 0.8% to 2.7%. Additionally, the discharge temperature of compressor and refrigerant charge of HFO-1234yf were lower than those of HFC-134a by about 6.5 C and 10%, respectively. Navarro-Esbrí et al. [10] compared the energy performance of HFO-1234yf and HFC-134a in a vapor compression system under various working conditions. The results indicated that HFO-1234yf had a lower cooling capacity and COP than HFC-134a by about 9% and 19%, respectively, but using an internal heat exchanger reduced these differences. Mota-Babiloni et al. [11] experimentally assessed the energy performance of HFO-1234yf and HFO-1234ze (E) as drop-in replacements for HFC-134a in a monitored vapor compression system with and without an internal heat exchanger. They found that without an internal heat exchanger, the volumetric efficiency and COP of HFO-1234yf and HFO-1234ze (E) were lower than those of HFC-134a by 4% to 5% and 6% to 7%, respectively. Jankovic et al. [12] analyzed the performance of HFO-1234yf and HFO-1234ze (E) as drop-in replacements for HFC-134a in a small power refrigeration system and developed a simulation model validated with test data. Their results indicated that HFO-1234yf is a suitable drop-in refrigerant for HFC-134a, but HFO-1234ze (E) could perform better when an overridden compressor was used. Finally, P. Arora et al. [13] presented a comprehensive review of different refrigerants and recommended HFO-1234yf as a fourth-generation refrigerant.

Based on previous theoretical and experimental studies, limited research has been conducted in the area of HFO-1234yf, with only a few theoretical papers [14, 15] and the majority of work being experimental. The current literature survey suggests that no investigations of inter- and intra-molecular interactions using vibrational spectroscopic methods have been reported to date. Therefore, the present study aims to perform B3LYP/6-311++G(d,p) level of theory calculations on HFO-1234yf molecule and investigate various molecular properties, such as molecular electrostatic potential (MEP) mapping and HOMO-LUMO analysis of the title molecule, which is an environmentally friendly refrigerant, by simulating the components of an automotive air conditioning system.

Computational Details
The Gaussian 03 program package [16] was utilized for all quantum chemical calculations. The geometry of the studied molecule was fully optimized without any symmetry constraints. Density functional theory (DFT) with the Becke's three-parameter hybrid functional B3LYP using the standard basis set 6-311++G (d,p) was employed to calculate the optimized geometrical structures in the gas phase and vibrational wavenumbers of different normal modes [17-19]. The obtained vibrational wavenumbers for the optimized structure of the title molecule were only real and confirmed that the optimized geometry was the global minima on the potential energy surface. The results were consistent with the experimental data, accounting for the anharmonicity effect found by Jan Schwabedissen et al [15]. The normal modes assignment was verified, and visual animations were generated using the GaussView program [20].

2. Results and Discussions

1) Molecular geometry
The molecular geometry of HFO-1234yf was determined through computational calculations. The calculated values of bond lengths, bond angles, and dihedral angles were used as the basis for determining other parameters such as vibrational frequency. The C=C bond length between atoms C1 and C2 was calculated to be 1.3196 Å, while the C–C bond length between C1 and C5 was calculated to be 1.5087 Å. These values are in good agreement with the experimental values of 1.304(7) Å and 1.490(6) Å, respectively. The calculated bond lengths and bond angles were also found to be in good agreement with experimental data. The molecular structure of HFO-1234yf, along with atom numbering, is shown in Figure 1. These results demonstrate that the calculated molecular geometry of HFO-1234yf provides a satisfactory approximation of its actual structure.

Table 1: The Optimized Geometrical Parameters (Bond Lengths, Bond Angles and Dihedral Angles) of HFO-1234yf obtained by B3LYP/6-311++G(d,p) Basis Set[14]

Bond Length	Value (A^0) Calculated	*Value (A^0) Experimental	Bond Angles	Calculated (in Degrees)	*Experimental (in Degrees)	Dihedral Angles	Degrees (Experimental Values)
R(C1-C2)	1.3196	1.304(7)	A(C2-C1-C5)	126.15	126.5	D(C5-C1-C2-H3)	-179.9993
R(C1-C5)	1.5087	1.490(6)	A(C2-C1-F6)	122.75	123.6	D(C2-C1-C5-F7)	120.2715
R(C1-F6)	1.3453	1.343 (5)	A(C5-C1-F6)	111.10	109.9	D(C2-C1-C5-F8)	-120.2768
R(C2-H3)	1.0817	-	A(C1-C2-H3)	120.49	-	D(C2-C1-C5-F9)	-0.00 (-0.5)*
R(C2-H4)	1.0797	-	A(C1-C2-H4)	120.06	-	D(F6-C1-C5-F7)	-59.7284
R(C5-F7)	1.3480	1.325(5)	A(H3-C2-H4)	119.43	-	D(F6-C1-C5-F8)	59.72 (58.2)*
R(C5-F8)	1.3480	1.350(6)	A(C1-C5-F7)	111.24	112.1	D(F6-C1-C5-F9)	179.9 (178.7)*
R(C5-F9)	1.3453	1.339(5)	A(C1-C5-F8)	111.24	111.3		
			A(C1-C5-F9)	111.18	111.8		
			A(F7-C5-F8)	107.21	107.6		
			A(F7-C5-F9)	107.89	107.9		
			A(F8-C5-F9)	107.89	105.9		

Figure 1: Optimized molecular structure of HFO-1234yf along with numbering of atoms at B3LYP/6-311++G(d,p) Basis Set

2) Vibrational assignments

The molecular vibrations of the title molecule, which contains 9 atoms, were studied using harmonic vibrational frequency calculations at the DFT B3LYP level with the 6-311++G(d, p) basis set including diffuse and polarization functions. A total of 21 normal modes of vibration were identified and their corresponding frequencies were presented in Table 2. The calculated vibrational frequencies were found to be in good agreement with the experimental values reported in literature [14], with the exception of anharmonic effects that were not accounted for in the DFT calculations. The normal modes assignments were verified using the Gauss View program and visual animations were obtained. The FT-IR spectra of the title molecule were calculated at the DFT/B3LYP level using the same basis set and compared with the observed spectra, as shown in Figs. 2 and 3, respectively. Overall, these results provide a comprehensive understanding of the molecular vibrations of the title molecule and can be used for future investigations of its properties and reactivity.

Table 2: B3LYP/6-311++G(d,p) level calculated vibrational frequency (cm^{-1}), IR Intensity (Km mol^{-1}), Raman intensity (A^4amu^{-1}), Reduced masses (amu), force constants (m dyne A^{-1}), depolarization ratios for HFO-1234yf [14]

No.	Calculated wavenumbers (cm^{-1})	Experimental* wavenumbers (cm^{-1})	IR intensity	Raman intensity	Reduced mass	Force constant	Depolar (P)	Depolar (U)	[a]PED (%) among type of internal coordinates
1	3277	-	1.03	44.13	1.12	7.07	0.75	0.86	υCH (99)
2	3178	3055	3.75	95.69	1.06	6.32	0.13	0.23	υCH (99)
3	1746	1700	50.67	39.22	6.88	12.36	0.11	0.20	υCC(63),
4	1416	1391	39.43	12.99	1.22	1.45	0.42	0.60	υCC (53), bCH (41)
5	1350	1357	147.37	0.82	5.73	6.16	0.65	0.79	-
6	1170	1210	336.22	2.13	12.79	10.33	0.44	0.61	bCH(64), υCC (32)
7	1143	1190	204.22	0.20	4.95	3.81	0.39	0.56	υCC(22), bCH(12)
8	1134	1181	338.55	3.02	12.12	9.19	0.75	0.85	υCC (62)
9	950	945	26.21	3.85	2.16	1.15	0.36	0.53	gCH(86)
10	932	889	49.45	2.11	1.35	0.69	0.75	0.85	υCC(10)
11	781	793	2.65	9.59	9.61	3.46	0.03	0.06	b CF (13)
12	753	-	0.75	0.84	1.09	0.36	0.75	0.85	gCH(14)
13	674	615	0.41	0.25	7.55	2.02	0.75	0.86	gCF (17), gCH (11)
14	608	579	22.84	2.21	6.36	1.39	0.39	0.57	-
15	568	-	6.82	1.45	6.68	1.27	0.62	0.77	υCF (39)
16	492	-	0.62	1.68	11.65	1.66	0.75	0.86	gCF(12)
17	415	-	1.58	1.90	10.25	1.04	0.72	0.84	gCH (19)
18	364	-	0.61	2.48	4.28	0.33	0.49	0.66	bCF(46)
19	235	-	0.03	1.96	8.12	0.26	0.75	0.86	υCF (49)
20	235	-	1.29	0.21	9.41	0.31	0.60	0.75	bCF(48)
21	65	-	1.44	1.52	7.16	0.02	0.75	0.86	gCH(19)
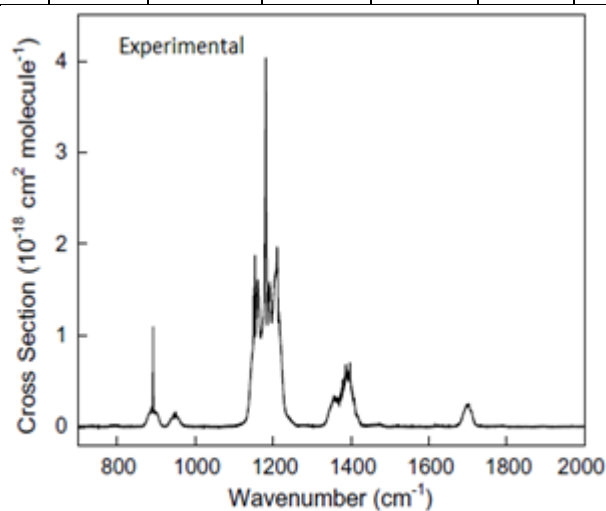
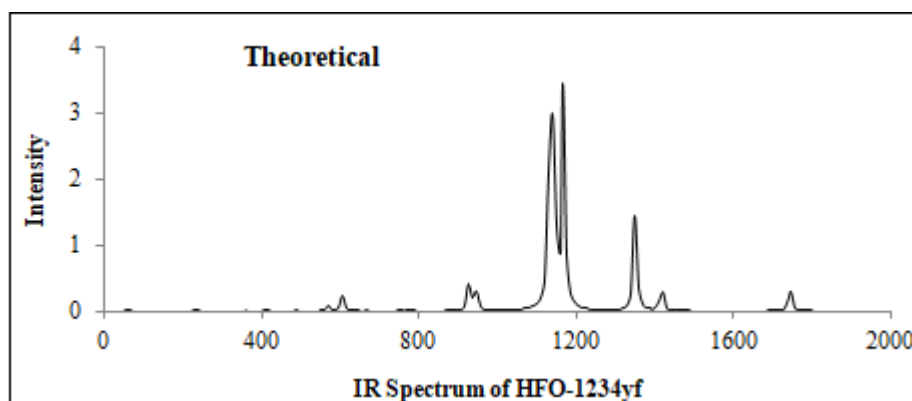**Figure 2:** Experimental IR spectra of HFO-1234yf [5]

Figure 3: Theoretical IR spectra of HFO-1234yf

3) Mulliken Atomic Charges

The calculation of Mulliken atomic charges is an essential component of quantum chemical calculations of molecular systems, as the distribution of atomic charges plays a crucial role in determining various properties such as dipole moment, polarizability, and electronic structure. The charge distribution also provides insight into the formation of donor-acceptor pairs and charge transfer within the molecule. In this study, Mulliken and natural charge distributions for the HFO-1234yf molecule were calculated using the B3LYP method with the 6-311++G(d,p) basis set. The calculated Mulliken Atomic Charges, along with atom numbering, are shown in Fig. 2 and the corresponding values are listed in Table 3. These results provide valuable information regarding the charge distribution within the molecule and can be used to understand its electronic structure and reactivity.
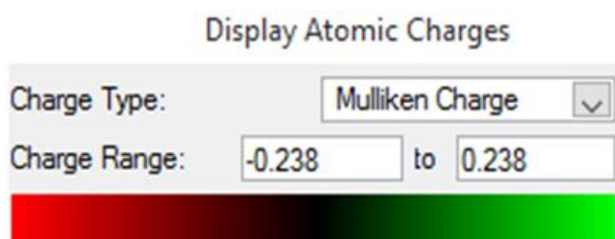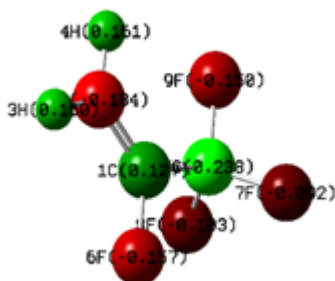

Figure 4: Optimized molecular structure of HFO-1234yf along with numbering of atoms and calculated Mulliken Charges at B3LYP/6-311++G(d,p) Basis Set

Table 3: Mulliken Atomic Charges of HFO-1234yf

Atom	Mulliken atomic charges
1 C	0.126987
2 C	-0.184185
3 H	0.160096
4 H	0.161117
5 C	0.237950
6 F	-0.157321
7 F	-0.091863
8 F	-0.102954
9 F	-0.149827

4) Molecular Electrostatic Potential

The molecular electrostatic potential (MEP) is a measure of the potential energy that a unit positive charge would experience at any point surrounding a molecule due to the electron density distribution in the molecule. It is a useful tool for understanding the electrophilic and nucleophilic regions in the molecule. The electrostatic potential map provides a three-dimensional illustration of the charge distribution in the molecule, allowing for a better understanding of how molecules interact with each other. MEP mapping is valuable in investigating the physiochemical properties of the molecular structure. In the case of HFO-1234yf, the electrostatic potential map shows semispherical blue shapes that represent hydrogen atoms. The molecular electrostatic potential surface (MESP), which is a 3D plot of electrostatic potential mapped onto the iso-electron density surface, displays the molecular shape, size, and electrostatic potential values simultaneously. The electrostatic potential surface of HFO-1234yf is shown in Figure 5, providing valuable information about its electrostatic properties and aiding in the investigation of its reactivity and other properties.
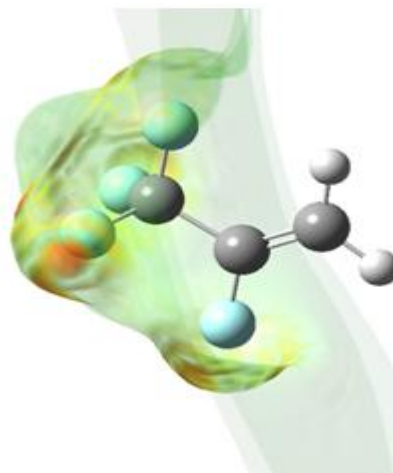

Figure 5: The Electrostatic potential surface of HFO-1234yf

Total electron density iso surface mapped with molecular electrostatic potential of HFO-1234yf with different views like a) solid view b) mesh view and c) transparent view are shown in Figure 6.
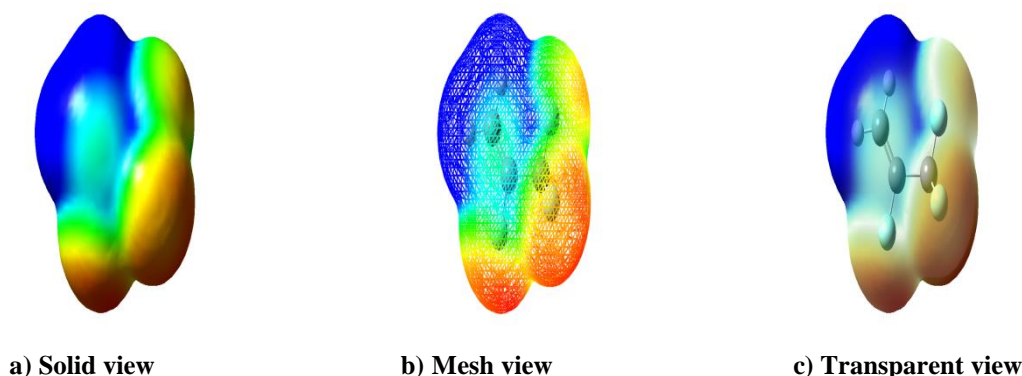

a) Solid view **b) Mesh view** **c) Transparent view**

Figure 6: Total electron density isosurface mapped with molecular electrostatic potential of HFO-1234yf

The molecular electrostatic potential (MESP) surface of HFO-1234yf reveals valuable information about the electronic properties of the molecule. The color scheme used to represent the MESP surface is as follows: red indicates an electron-rich or partially negative charge; blue indicates an electron-deficient or partially positive charge; light blue indicates a slightly electron-deficient region; and yellow indicates a slightly electron-rich region. The MESP surface indicates that areas of low potential, shown in red, are characterized by an abundance of electrons, while areas of high potential, shown in blue, are characterized by a relative absence of electrons. In the case of HFO-1234yf, negative potential sites are found on the electronegative atoms like fluorine, while the positive potential sites are located around the hydrogen and carbon atoms. The green region on the MESP surface covers the parts of the molecule where electrostatic potentials are nearly equal to zero, such as the C-C bond. This region of zero potential envelops the π systems of the aromatic ring, leaving a more electrophilic region in the plane of the hydrogen atom. As nitrogen has a lower electronegativity value, it consequently has a lower electron density around it. Therefore, the spherical region that corresponds to the nitrogen atom would have a green portion on it. Overall, the MESP of HFO-1234yf clearly indicates the electron-rich centers of fluorine and oxygen and the areas covering them. The total electron density iso surface mapped with molecular electrostatic potential of HFO-1234yf with different views, including solid view, mesh view, and transparent view, are shown in Figure 6.

5) HOMO - LUMO Analysis

In quantum chemistry, the interaction between molecular orbitals is crucial in determining the properties of molecular systems. The two molecular orbitals that typically interact are the Highest Energy Occupied Molecular Orbital (HOMO) of one molecule and the Lowest Energy Unoccupied Molecular Orbital (LUMO) of the other molecule. These orbitals are often referred to as the frontier orbitals as they lie at the outermost boundaries of the electron distribution of the molecules. The energy difference between the HOMO and LUMO, known as the energy gap, is a crucial parameter in determining the electron conductivity and molecular chemical stability. The HOMO characterizes the ability of electron donating, while the LUMO characterizes the ability of electron accepting. In this study, surfaces for the frontier orbitals were generated to gain insights into the bonding scheme of the HFO-1234yf molecule. The features of these molecular orbitals are depicted in Figure
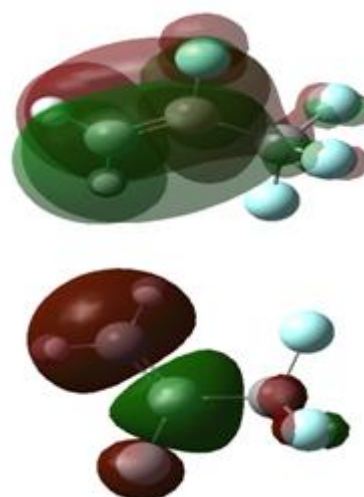

Figure 7: HOMO LUMO plot of HFO-1234yf

This electronic absorption corresponds to the transition from the ground state to the first excited state and is mainly described by one electron excitation from HOMO to LUMO. While the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. There are lots of applications available for the use of HOMO and LUMO energy gap as a quantum chemical descriptor. It establishes correlation in various chemical and bio-chemical systems. The HOMO–LUMO energy gap is an important value for stability index. A large HOMO–LUMO gap implies high stability for the molecule in the sense of its lower reactivity in chemical reactions. According to B3LYP/6-311G++(d,p) calculation, EHOMO , ELUMO and the energy band gap (translation from HOMO to LUMO) of the title molecule in electron Volt are presented in Table 4.

Table 4: HOMO-LUMO Energy and Energy Gap of HFO-1234yf

Energies	Values
EHOMO (e V)	-8.53
ELUMO (eV)	-1.32
EHOMO–ELUMO gap e V	-7.21

3. Conclusion

Based on analysis, 2, 3, 3, 3-Tetrafluoropropene (HFO-1234yf) is a viable, environmentally-friendly refrigerant option for use in mobile air-conditioning (MAC) systems. Its chemical composition, $CF_3CF=CH_2$, is well-defined, and it presents a feasible alternative to HFC-134a in the automotive industry. While HFO-1234yf exhibits mild flammability, its low burning velocity and high minimum ignition energy make it a safe option for mobile air-conditioning. HFO-1234yf is also compatible with various materials and exhibits good thermal stability. The oxidation of HFO-1234yf yields TFA, which is not expected to have significant environmental impacts, but can be toxic to aquatic life. Our density functional theory (DFT) calculations using the B3LYP/6-311++G(d,p) levels allowed for the determination of various molecular properties such as ground state molecular geometry, harmonic vibrational wavenumbers, infrared intensities, Raman activities, and HOMO-LUMO analysis, revealing significant charge transfer interactions. This technique proves to be a valuable tool for non-experts to interpret key experimental properties of molecules with high accuracy. In conclusion, HFO-1234yf can safely and effectively be used in refrigeration and air-conditioning applications in mobile and stationary systems with minimal changes in vehicle design, engineering, and manufacturing.Based on the results of this study, it can be concluded that 2,3,3,3-Tetrafluoropropene (HFO-1234yf) is an environment-friendly refrigerant with zero ozone depletion potential (ODP) and very low global warming potential (GWP), making it a suitable replacement for HFC-134a in mobile air-conditioning (MAC) systems. Despite its mild flammability, HFO-1234yf exhibits low burning velocity and high minimum ignition energy, making it safe for use in MAC systems. It is also compatible with various materials and lubricants and demonstrates good thermal stability. Although atmospheric oxidation of HFO-1234yf produces TFA, which is toxic to aquatic life, it does not bioaccumulate and is not phytotoxic. This study also highlights the usefulness of density functional theory (DFT) calculations, specifically the B3LYP/6-311++G(d,p) level, in determining the molecular geometry, vibrational frequencies, and electronic properties of HFO-1234yf. The HOMO-LUMO analysis reveals the presence of charge transfer interactions that contribute to the molecule's properties. Therefore, HFO-1234yf can be safely used in refrigeration and air-conditioning applications in mobile and stationary systems with minimal changes to vehicle design, engineering, and manufacturing.

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