



## Comparative Computational Study on Molecular Structure, Electronic and Vibrational Analysis of Vinyl Bromide based on HF and DFT Approach

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### Abstract

In this study, we have used the Hartree-Fock and Density Functional Theory method of calculation and compared the equilibrium configuration, electronic and vibrational mode of Vinyl Bromide molecule. The molecule is geometrically optimized initially by using 6-31G basis set with B3LYP functional and then bond angles, bond lengths, dihedral angles and IR spectra are compared respectively. Various groups of atoms in Vinyl Bromide molecule by DFT has more accurate bond length, bond angle values rather than by HF computation when comparing with the experimental values. The ground state energies are found at angle 10° or 180° or 360° using HF and DFT method of calculation for the H4-C1-C2-Br6 position. Values of the carbon-hydrogen, carbon-carbon and carbon-bromine bond lengths and bond angles for optimization state of C<sub>2</sub>H<sub>3</sub>Br molecule using Hartree-Fock and Density Functional Theory methods with respect to the basis set 6-31G have been analyzed. The C–H in-plane bending vibration and C–H out-of-plane bending vibrations occur in the region 1400–1050 cm<sup>-1</sup> and 1000–675 cm<sup>-1</sup> respectively. The electronic properties, such as Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital energies are performed by HF and DFT approach and the difference in Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital energy gap for HF and DFT method are 14.0847 eV and 6.8994 eV respectively.

### 1. Introduction

Vinyl Bromide (VB) or 1-Bromoethene (H<sub>2</sub>C=CHBr) is a colorless gas which is produced from ethylene dibromide. It lies in the member of the vinyl halide class. Vinyl halides are monohalogen derivatives of alkanes in which the halogen atom is attached to carbon carrying the double bond. VB (C<sub>2</sub>H<sub>3</sub>Br) has molecular weight of 106.95 g/mol and is also known as Bromoethylene or monobromoethylene (Coffey et al., 1993). It is mainly used as a flame retardant in acrylic fibers. It is also used in the production of polyvinyl bromide and other bromopolymers or polymers in the production of fabrics and home furnishing, in lather and fabricated metal products (Mathews, 1996;

Feldman & Barbalata, 1993; Tonelli, 1982). VB is a recognized as carcinogen and liver toxicant. This molecule is reasonably anticipated to be a human carcinogen based on evidence of tumor induction at multiple organ sites in rats (Zvereva-Loete et al., 2006; Calnan, 1963). Figure 1 shows chemical structure of VB and its chemical structure includes the arrangement of atoms and the chemical bonds that hold the atoms together. VB molecule contains a total of 5 bond(s). There are 2 non-H bond(s), 1 multiple bond(s), and 1 double bond. Its low-resolution infrared spectrum has been recorded a long time ago and all fundamental vibrations are assigned (Gullikson & Nielsen, 1957). The utilization of Monte Carlo simulation, as detailed in reference (Gauli et al., 2023), offers a method for studying hydrogenated

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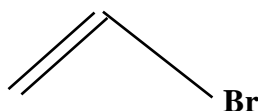
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poly(vinyl halides) (HPVH). The reaction dynamics of vibrationally excited VB using classical trajectory methods and electronic structure calculations have been conducted at the Moller Plesset (MP4) level of theory using a 6-31G(d,p) basis set for the carbon and hydrogen atoms (Doughan et al., 2006). Intra-molecular energy transfer rates and pathways for VB has also been observed (Pan & Raff, 1996).



**Figure 1:** Chemical structure of Vinyl Bromide ( $C_2H_3Br$ )

Over the decade many calculations of various heavy molecules have been done and useful properties of many electron problems were identified using the *ab initio* methods. But the literature survey reveals none of the quantum chemical calculations of optimization energy, bond length, bond angle, dihedral angle, IR spectroscopy and energy gap for VB molecule have been reported so far. So, this study aims to investigate the equilibrium configuration, ground state energy, bond lengths, bond angles, dihedral angles, IR spectra and energy gap of VB in which these obtained values from Hartree-Fock (HF) and Density Functional Theory (DFT) are compared. In addition to these, we have also presented molecular electrostatic potential surface (MEP), electrostatic potential (ESP), electron density (ED), highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbital (LUMO) using *ab initio* HF and DFT methods.

## 2. Computational Details

In the present work, First-principles study of the equilibrium configuration, vibrational analysis, MEP, ESP, ED, HOMO and LUMO of VB molecule were carried out using Gaussian 09 (Frisch et al., 2009) sets of software packages together with a concept of 6-31G basis set based

on Becke's three parameter (local, non-local, Hartree-Fock) hybrid exchange functional with Lee-Yang-Parr correlation functional (B3LYP). Gaussian 09W is a general-purpose *ab initio* electronic structure package which can predict many properties of molecules and reaction pathways based on various uncorrelated and correlated wave function. Gaussian calculations were best prepared using the GaussView 6.0 interface. GaussView 6.0 allowed to build the required molecule on screen using menu and by selecting the required type (optimization, energy, frequency and many other) and then selecting the desired *ab initio* methods, the molecule containing respective file name was submitted into the Gaussian09 program for execution. After the Gaussian run progress, the .log file written by Gaussian and the binary .chk file to generate various graphical surfaces were obtained. The .log file information written in text and .chk (checkpoint) file with generated various surface representation and various results were checked out (Sack, 2017).

## 3. Results and discussion

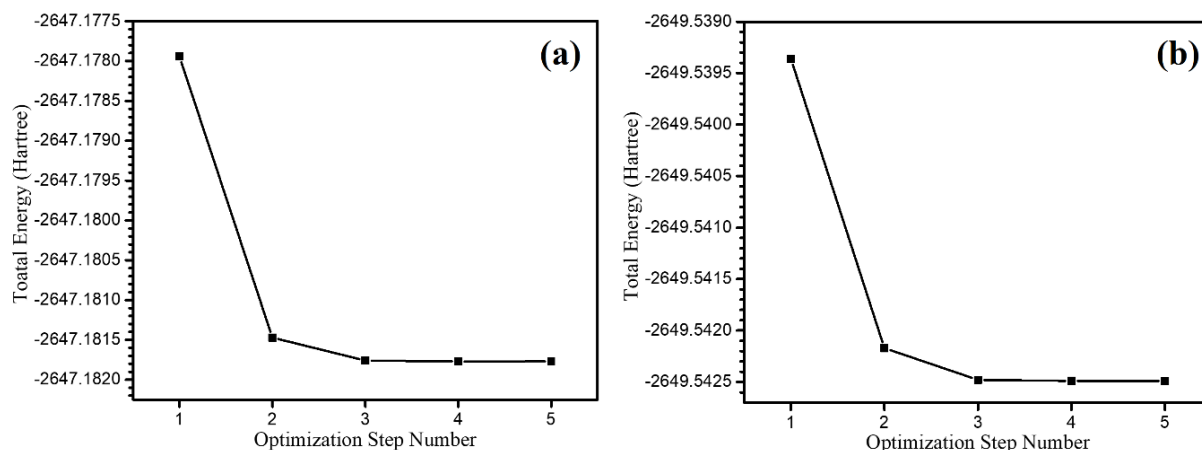
### 3.1 Geometry Optimization

Figure 2 shows the optimized structure of VB molecule. The equilibrium geometry was determined by the energy minimization. Energy minimization is essential to find a set of coordinates representing the minimum energy conformation for the given structure. Gaussian calculation was set up using charge value 0 (neutral). At the Becke's three parameter (local, non-local, Hartree-Fock) hybrid exchange functional with Lee-Yang-Parr correlation functional (B3LYP), the optimization energy of the molecule was calculated using the HF and DFT method respectively using basis sets 6-31G.

Figures 3(a) and 3(b) respectively show that the HF and DFT calculation plot between total energy versus optimization step number of VB molecule to be in the optimization state. We see that the total optimization energy takes place in

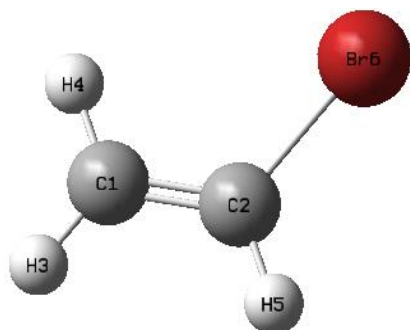
the five states both by HF and DFT calculations.

In HF method, the optimization step starts from



**Figure 3:** Plot for optimization step number vs total energy using (a) HF and (b) DFT method

the energy of -2647.17794 Hartree and gets optimized in the energy -2647.181768 Hartree whereas in DFT, VB molecule starts from the energy of -2649.53936 Hartree and gets optimized in the energy -2649.542491 Hartree. From both the figures, we see that there are altogether five set of coordinates representing required to set stable energy conformations for VB molecule.



**Figure 2:** Optimized structure of VB ( $C_2H_3Br$ ) using DFT (Carbon: gray, Hydrogen: white and Bromine: red in color).

### 3.2 Minimum Energy Calculation for the Equilibrium Configuration

To calculate the ground state energy for VB molecule with respect to dihedral angle, we have set the dihedral angle in the position of H4-C1-C2-Br6 and rotate the dihedral angle  $10^\circ$  to  $360^\circ$  degree in the interval of  $10^\circ$ . Following the methodology, we have plotted a graph between energy and dihedral angle, using

X-axis as angle and Y-axis as energy in eV. The figure 4 shows the different possible energy values at different possible dihedral angles. From this figure, we have chosen only the possible minimum energy level known as the ground state energy corresponding through angles for successful result. The energy of each dihedral angle is estimated in Hartree and atomic units (a. u.) and then converted to electron volts (eV) using the formula i.e. 1 Hartree = 27.2114 eV and 1 a. u. = 27.2114 eV (Energy Conversion Table, 2018). Different energy values of VB molecule for different dihedral angles is summarized in the table 1.

The relationship between dihedral angle along X-axis and energy in eV along Y-axis is shown in figure 4. Figure 4 shows that the energy values for HF method are -72027.46628 eV for  $90^\circ$  and -72027.46628 eV for  $270^\circ$ . Similarly, the energies for DFT method are -72093.44691 eV and -72093.44691 for  $90^\circ$  and  $270^\circ$  respectively. From these values, HF and DFT methods result in a total energy difference of  $(-72027.46628 + 72093.44691)$  eV = 65.98063 eV. The graph in figure 4 also indicates that the minimum energy at  $10^\circ$ ,  $180^\circ$  and  $360^\circ$  for both HF and DFT known as the ground state energy and molecule's energy varies depending on the dihedral angle. There are local minima and maxima in several angles. At a dihedral angle of  $10^\circ$ ,  $180^\circ$  and  $360^\circ$ , the minimal ground state

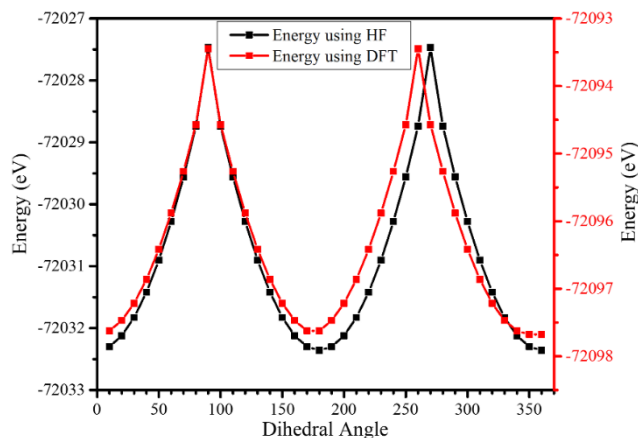
energies are obtained. As a result, the structure with the dihedral angle of 10°, 180° and 360° for HF and DFT are the most stable state. So,

involving 10° or 180° or 360° as dihedral angle is required in optimization state, and it is possible by selecting dihedral angle in the position of

**Table 1:** Energy of Vinyl Bromide (C<sub>2</sub>H<sub>3</sub>Br) at various dihedral angles by HF and DFT

Angle (°)	HF		DFT	
	Energy (Hartree)	Energy (eV)	Energy (a. u.)	Energy (eV)
0	-2647.177944	-72032.35903	-2649.539358	-72097.67529
10	-2647.175759	-72032.29958	-2,649.537463	-72097.62373
20	-2647.169229	-72032.12189	-2,649.531801	-72097.46966
30	-2647.158421	-72031.82779	-2,649.522441	-72097.21496
40	-2647.143436	-72031.42004	-2,649.509491	-72096.86257
50	-2647.1244	-72030.90205	-2,649.493087	-72096.41621
60	-2647.101474	-72030.27821	-2,649.473404	-72095.88059
70	-2647.074874	-72029.5544	-2,649.450674	-72095.26209
80	-2647.044923	-72028.7394	-2,649.425248	-72094.57021
90	-2646.998136	-72027.46628	-2,649.383968	-72093.44691
100	-2647.044923	-72028.7394	-2,649.425248	-72094.57021
110	-2647.074874	-72029.5544	-2,649.450674	-72095.26209
120	-2647.101474	-72030.27821	-2,649.473404	-72095.88059
130	-2647.1244	-72030.90205	-2,649.493087	-72096.41621
140	-2647.143436	-72031.42004	-2,649.509491	-72096.86257
150	-2647.158421	-72031.82779	-2,649.522441	-72097.21496
160	-2647.169229	-72032.12189	-2,649.531801	-72097.46966
170	-2647.175759	-72032.29958	-2,649.537463	-72097.62373
180	-2647.177944	-72032.35903	-2,649.537463	-72097.62373
190	-2647.175759	-72032.29958	-2,649.531801	-72097.46966
200	-2647.169229	-72032.12189	-2,649.522441	-72097.21496
210	-2647.158421	-72031.82779	-2,649.509491	-72096.86257
220	-2647.143436	-72031.42004	-2,649.493087	-72096.41621
230	-2647.1244	-72030.90205	-2,649.473404	-72095.88059
240	-2647.101474	-72030.27821	-2,649.450674	-72095.26209
250	-2647.074874	-72029.5544	-2,649.425248	-72094.57021
260	-2647.044923	-72028.7394	-2,649.383968	-72093.44691
270	-2646.998136	-72027.46628	-2,649.425248	-72094.57021
280	-2647.044923	-72028.7394	-2,649.450674	-72095.26209
290	-2647.074874	-72029.5544	-2,649.473404	-72095.88059
300	-2647.101474	-72030.27821	-2,649.493087	-72096.41621
310	-2647.1244	-72030.90205	-2,649.509491	-72096.86257
320	-2647.143436	-72031.42004	-2,649.522441	-72097.21496
330	-2647.158421	-72031.82779	-2,649.531801	-72097.46966
340	-2647.169229	-72032.12189	-2,649.537463	-72097.62373
350	-2647.175759	-72032.29958	-2,649.539358	-72097.67529
360	-2647.177944	-72032.35903	2649.539358	-72097.67529

H4-C1-C2-Br6 group of VB molecule for further calculation of bond length and bond angles. Therefore those angles i.e.  $10^\circ$  or  $180^\circ$  or  $360^\circ$  as dihedral angle in which the VB molecule gets optimized and remains stable indicating less reactive at this degree of rotation of position of H4-C1-C2-Br6 group.



**Figure 4:** Plot between dihedral angle and energy

### 3.3 Calculation of Bond Lengths and Bond angle

Geometry optimization was used to find VB molecule's minimum energy structure. The chemical structure of VB in figure 1 has 2 carbon atoms, 3 hydrogen atoms, 1 bromine atom. Bond angles, bond lengths between these atoms were calculated from the optimized geometry structure of VB molecule using the HF and DFT. Table 2 gives the comparison between the calculated and experimentally (Haynes et al., 2014-2015) observed values of the bond lengths and bond angles for optimization state of VB molecule using HF and DFT method with respect to basis set 6-31G.

The average distance between two molecules participating in a bond is referred to as bond length. Bond length is determined based on the type of bond, such as hybridization, electronegativity difference and so on (Kaupp et al., 2017). In VB molecule, a bond length between Carbon-Carbon atoms was found to be

more accurate near to reported value by DFT method rather than by HF method. While both HF and DFT method overestimates the Carbon-Bromine bond length. But Carbon-Bromine bond length was found to be more accurate by HF in comparison to DFT. Similarly, HF method underestimate the Carbon-Hydrogen bond length, but DFT method gives accurate value of C-H bond length in VB molecule.

Bond angle, on the other hand, is the angle created by three atoms separated by at least two bonds. From the calculation and observations from table 2, it is appropriate to call that the bond angles created by various groups of three atoms in VB molecule by DFT has more accurate angle values rather than by HF computation when comparing with the experimental values. Many factors influence bond angle, including electronegativity, atom type, repulsion between bond pair and lone pair electrons, and hybridization type (Alabugin et al., 2015).

### 3.4 Calculation of Vibrational Property of Vinyl Bromide Molecule in Neutral Form

For the position of H4-C2-C1-Br6 group, the ideal dihedral angles for neutral  $C_2H_3Br$  are found to be at  $10^\circ$ ,  $180^\circ$  and  $360^\circ$ . As a result, this structure was used to calculate vibrational properties. Figures 5(a) and 5(b) show IR spectra of neutral VB molecule by HF and DFT method respectively. The interaction of matter with infrared radiation signifies the IR spectroscopy and it is a spectrum that shows the relationship between frequency and wavelength of infrared light (transmittance or absorption) (Khan, et al., 2018; Kohn, 1999, Rai, et al., 2022).

Every chemical bond oscillates with specific frequency that corresponds to certain amount of energy. The frequency of oscillation of any chemical bond is related to wavenumber that is given in unit per centimeter. The greater the frequency of oscillation of chemical bond greater is the wave function (Segneanu et al., 2012). By

using IR spectrum, it is distinguished that which chemical bond and possible functional groups oscillate with how much of specific frequency that corresponds to certain amount of energy for  $C_2H_3Br$  molecule. According to IR graph, X-axis is wave number and Y-axis is percentage

transmitted. Along the Y-axis less energy is transmitted, more is absorbed and along X-axis, increase in wave number increases frequency and energy of that oscillating chemical bond. The bond

**Table 2:** calculated and experimentally observed values of the bond lengths and bond angles of  $C_2H_3Br$  molecule

Method	Parameters		Calculated Values	Experimental Values [13]
HF	Bond Length in (Å)	C1-H3	1.071	1.080±0.001
		C1-H4	1.073	1.080±0.001
		C1-C2	1.313	1.332±0.001
		C2-H5	1.068	1.080±0.001
		C2-Br6	1.934	1.884±0.001
	Bond Angle in (°)	H3-C1-H4	117.32694	119.244
		H3-C1-C2	120.15642	119.472
		H4-C1-C2	122.51664	121.284
		H5-C2-Br6	112.59882	113.729
		C1-C2-Br6	122.01009	122.587
DFT (Basis set 6-31G)	Bond Length in (Å)	C1-H3	1.084	1.080±0.001
		C1-H4	1.086	1.080±0.001
		C1-C2	1.328	1.332±0.001
		C2-H5	1.081	1.080±0.001
		C2-Br6	1.950	1.884±0.001
	Bond Angle in (°)	H3-C1-H4	120	119.244
		H3-C1-C2	120	119.472
		H4-C1-C2	120	121.284
		H5-C2-Br6	120	113.729
		C1-C2-Br6	120	122.587
	C1-C2-H5	120	123.684	

located to the right one is stronger than that located at left. The peaks in the figures 5(a) and 5(b) are characteristic peaks which correspond to specific energy of the IR light that was absorbed or transmitted by the specific bond within VB molecule.

### C-H Vibration

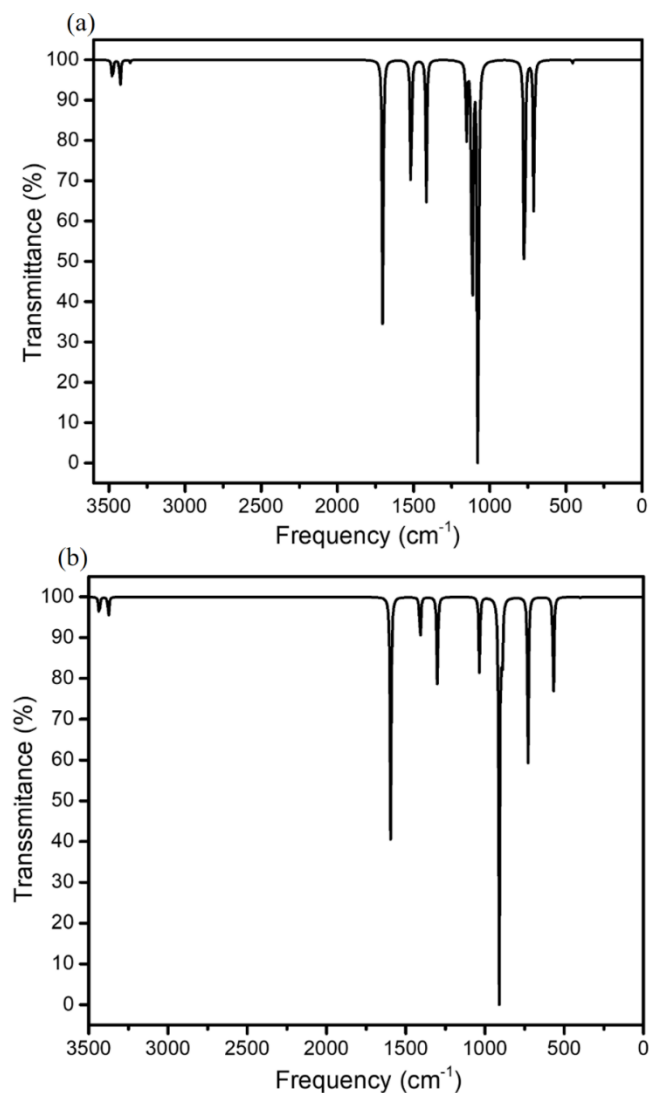
The C–H inplane bending vibration usually occurs in the region 1400–1050  $cm^{-1}$  and the C–H out of plane bending vibrations in the range 1000–675  $cm^{-1}$  (Balachandran et al., 2019). In DFT method of study, the IR spectra reveals the presence of C-H in-plane bending vibrations at

1011.17  $cm^{-1}$ , 1285.2895  $cm^{-1}$ , 1411.13  $cm^{-1}$ , and 1587.86  $cm^{-1}$ . Additionally, C-H out-of-plane vibrations are found at 547.7898  $cm^{-1}$ , 913.16  $cm^{-1}$ , and 924.21  $cm^{-1}$ . The C-H stretching vibrations exhibit symmetric stretching vibrations at 3376.5224  $cm^{-1}$  and 3311.90  $cm^{-1}$ , while the antisymmetric stretching vibration are observed at a frequency of 3432.3595  $cm^{-1}$  by DFT method. For HF method, the C-H in-plane bending vibrations are detected at 1135.36  $cm^{-1}$  and 1406.10  $cm^{-1}$ , while the C-H out-of-plane vibrations are observed at 690.98  $cm^{-1}$ , 1088.09  $cm^{-1}$ , and 1132.32  $cm^{-1}$ . Regarding the C-H stretching vibrations, the symmetric stretching

vibration occurs at  $3359.13\text{ cm}^{-1}$ , whereas the antisymmetric stretching vibrations are found at  $3426.37\text{ cm}^{-1}$  and  $3475.23\text{ cm}^{-1}$  by HF method.

### C=C Vibration

The ring C=C and C-C stretching vibrations usually occurs in the region  $1400\text{--}1625\text{ cm}^{-1}$  (Daswani et al., 2015). From the figures 5(a) and



**Figure 5:** IR spectroscopy for neutral VB ( $\text{C}_2\text{H}_3\text{Br}$ ) molecule by (a) HF and (b) DFT method

the frequency region  $650\text{--}480\text{ cm}^{-1}$ . The calculated C-Br stretching vibration is obtained at  $349.23\text{ cm}^{-1}$  by DFT and at  $399.50$  and  $640.13\text{ cm}^{-1}$  by HF method. C-Br bond shows lower absorption frequencies as compared to C-H bond due to the decreased force constant and increase

figure 5(b), the C=C vibrations are observed at  $1511.25$ ,  $1697.76\text{ cm}^{-1}$  by HF method and at  $1594.88\text{ cm}^{-1}$  by DFT method of calculation.

### C-Br Vibrations

The C-X (X = Br, Cl, I) vibrations are assigned in

in reduced mass (Arunagiri et al., 2011).

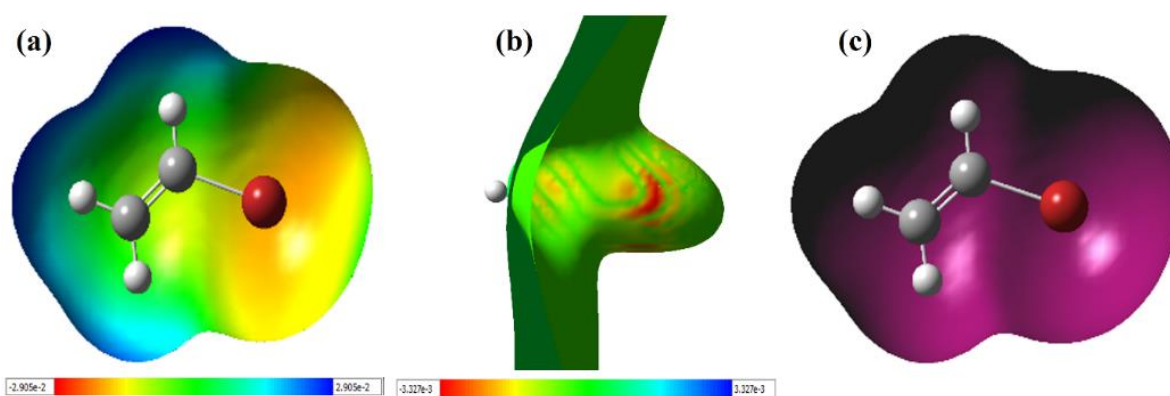
### 3.5 Molecular Electrostatic Potential (MEP), Electrostatic Potential (ESP) Surfaces and Electron Density (ED)

The MEP is reactivity map which shows the most probable regions for the electrophilic attack of charged point-like reagents on organic molecules (Yankova et al. 2016). The different values of the electrostatic potential at the surface are represented by different colors and increases in an order: red<orange<yellow<green<blue. Figures 6(a) and 7(a) show molecular electrostatic potential mapped on the isodensity surface in the range  $-2.905\text{e-}2$  (red) to  $+2.905\text{e-}2$  (blue) for HF and  $-2.711\text{e-}2$  (red) to  $+2.711\text{e-}2$  (blue) for DFT method. Both methods represent the negative potential localized over the Bromine atom that corresponds to the attraction of proton due the concentrated electron density and reflects by the yellowish region, while the positive potential is localized near the hydrogen atom which correspond to the repulsion of proton by low electron density and reflected by blue region. For ESP, the negative potential is localized near bromine atom due to the more electrophilic attack (yellowish region) while the positive potential is localized on the rest surface indicating nucleophilic attack as shown in figure 6(b) and 7(b) for respective HF and DFT method of calculations. Figures 6(c) and 7(c) correspond to the electron density (ED) plots of the VB molecule for HF and DFT methods of calculation and these show uniform charge distribution and the probability of an electron being present at the specific location.

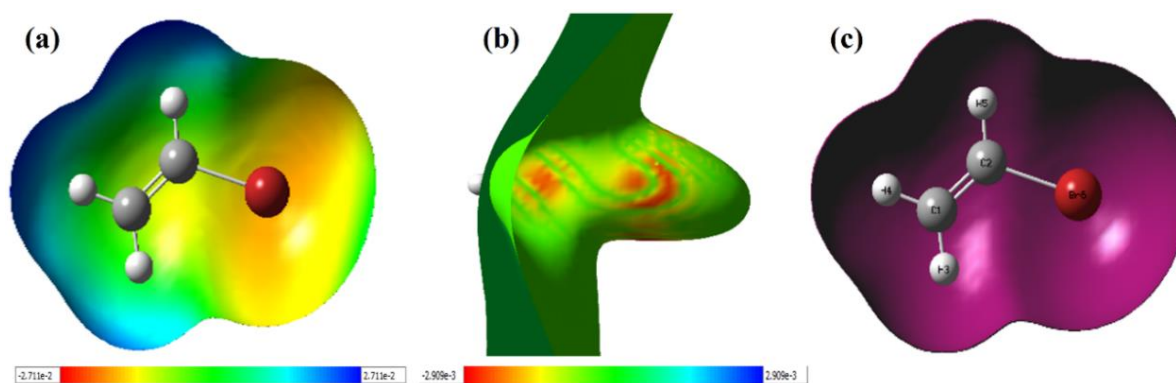
### 3.6 HOMO and LUMO Analysis

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 with isovalue 0.02. HOMO is outermost (higher energy) orbital containing electrons that could act as an electron donor. LUMO is the innermost orbital that has room to accept electrons and can act as the electron acceptor. The high value of HOMO indicates a tendency of the molecule to

donate electron to appropriate acceptor molecule of low empty molecular orbital energy. The lower values of LUMO energy show more probability to accept electron. (Joshi et al., 2021). According to the frontier molecular orbital (FMO) theory, the formation of a transition state is due to an interaction between the frontier orbitals (HOMO and LUMO) of reactants. The negative values of all the FMO energies indicate the stability of the

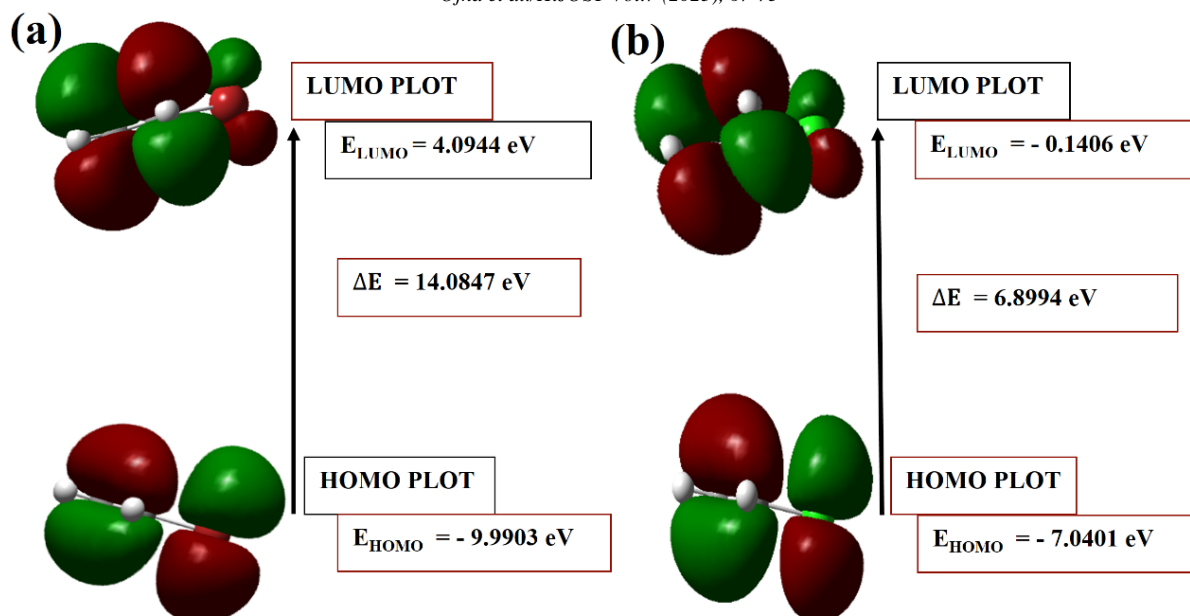


**Figure 6:** (a) molecular electrostatic potential (MEP) (b) electrostatic potential (ESP) (c) electron density (ED) of VB ( $C_2H_3Br$ ) molecule by HF method



**Figure 7:** (a) molecular electrostatic potential (MEP) (b) electrostatic potential (ESP) (c) electron density (ED) of VB ( $C_2H_3Br$ ) molecule by DFT method





**Figure 8:** Atomic orbital compositions of the frontier molecular orbital (HOMO-LUMO) by (a) HF and (b) DFT method

VB molecule (Joshi et al., 2013). The HOMO and LUMO energy calculated by B3LYP/6-31G method is shown in the table 3.

**Table 3:** HOMO and LUMO energy gap by HF and DFT

Molecular Orbital	HF method	DFT method
HOMO energy	-9.9903 eV	-7.0401 eV
LUMO energy	4.0944 eV	-0.1406 eV
HOMO-LUMO energy gap ( $\Delta E$ )	14.0847 eV	6.8994 eV

Figures 8(a) and 8(b) show the energies of two important molecular orbitals of VB molecule and they are the highest occupied molecular orbitals (HOMO) and the lowest unoccupied orbitals (LUMO) by (a) HF and (b) DFT method. The energy gap between HOMO and LUMO is an important stability index. A higher value of the energy difference more is the stability of the molecular system. Low gap value refers to 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 reactions (Arunagiri et al., 2011; Yankova et al., 2016; Joshi et al., 2021; Joshi et al., 2013). Figures 8(a) and 8(b) clearly indicate

charge accumulated from HOMO to LUMO. In HOMO, the charge is accumulated at C-H as well as bromine atom in equal amount while in LUMO the charge accumulation is more at C-H than that at Bromine atom of the titled molecule. Also, it is observed that the energy gap value is higher by HF i.e. 14.0847 eV than that by DFT method i.e. 6.8994 eV.

#### 4. Conclusion

In this study we have observed VB molecule's structural, electronic and vibrational modes. The energy of neutral VB is computed at various dihedral angles. HF and DFT methods have different energy with respect to the change in dihedral angle. The structure with minimum energy, i.e., the structure with a dihedral angle of  $10^\circ$ ,  $180^\circ$  and  $360^\circ$ , is found to be the most stable indicating less reactive at this degree of rotation of position of H4-C1-C2-Br6 group. Comparison made between total energy for HF and DFT methods, resulting in a total energy difference of 65.98063 eV. The bond lengths, bond angles are all examined by computation and found that HF underestimates the result whereas DFT is more accurate to the experimental values of bond length and bond angle. Gaussian computation

was set up with a charge of 0 (neutral) to obtain the vibrational spectra of neutral VB. The region between 1400 and 1050  $\text{cm}^{-1}$  exhibits the C–H in-plane bending vibration, while the C–H out-of-plane bending vibrations can be observed in the region of 1000–675  $\text{cm}^{-1}$ . Information about the shape, size of electron density and the structure-activity relation have been analyzed by mapping MEP as well as ESP. The large value of the energy gap i.e. 14.0847 eV is obtained from the HOMO and LUMO analysis for HF method. It is found that in comparison to the HF model of computation, DFT method gives more accurate data of various calculations. It is so because of the exchange-correlation potential term that give wholesome interaction for each number of electrons with the help of density functional.

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### Conflicts of Interest

The authors report no conflicts of interest for this research work.

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