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RESEARCH ARTICLE

DENSITY FUNCTIONAL ANALYSIS OF 1,4-DIVINYLCYCLOHEXENE UNDER EXTERNAL ELECTRIC FIELD

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ABSTRACT

The Au and thiol substituted 1,4-divinylcyclohexene molecule has been studied for the zero field and various levels of applied external electric fields (EFs) using Density functional theory (DFT). The variation in bond length, variation in atomic charges calculated from MPA and NPA methods, reduction of HOMO-LUMO gap (HLG) and the increase of electric dipole moment with the increase of external EFs (from zero to 0.21 VÅ⁻¹) of the molecule have been analyzed. From the isosurface representation of molecular orbitals, it is clear that all the atoms of 1,4-divinylcyclohexene molecule between the two terminal thiol atoms are not delocalized. Hence, in this molecular system, even though small HLG exists for higher applied field, the possibility of conduction through the molecule is found to be very less, therefore, almost it acts as an insulator.

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INTRODUCTION

In "moletronic" systems, molecules perform the functions of electronic components (Tour, 1996; Cao and Brinker, 2006 and Michael Rieth and Wolfram Schommers, 2006). To be able to measure and understand the electrical properties of devices fabricated from electrically-active molecules, it is important to understand the intrinsic properties such as its length, conformation, energy gap between its frontier orbitals and its alignment to the Fermi level of metal atom (Cao and Brinker, 2006; Michael Rieth and Wolfram Schommers, 2006 and Peköz and Erkoç, 2007). Charge transport occurs in a moletronic system when a molecular orbital comes into resonance with the Fermi-level of a metal contact to which a voltage has been applied. These energy levels have been extensively investigated using *ab initio* calculations of isolated molecules. In addition, the charge transfer ability of a molecule also depends on the nature of the interaction between the molecule and the electrode, and the type of electrode materials (Peköz and Erkoç, 2007; Denille Brito de Lima and Jordan Del Nero, 2008; Antonis N. Andriotis *et al.*, 2008; Cai *et al.*, 2004; Luo *et al.*, 2011). The highest occupied molecular orbital HOMO, the lowest unoccupied molecular orbital (LUMO) are the frontier orbitals, the difference between them are known as HOMO-LUMO gap (HLG).

The HLG is directly linked to the extent of bond length alternation, (Geng *et al.*, 2008 and Kushmerick *et al.*, 2002) which is one of the key factor to find out the transport properties of the molecule. Large decrease in the HLG predicts the possibility of having reasonable conduction through the molecule, since, the conductivity increases with decrease in HLG.

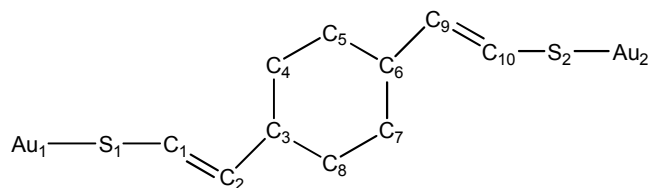


Fig. 1. Au and S substituted 1,4-divinylcyclohexene (DVCH) molecule

In the present study, electrostatic and transport properties of Au and thiol substituted 1,4-divinylcyclohexene (DVCH) molecule (Fig.1) has been studied for various applied electric fields (EFs) using Density functional theory. Here, thiol atoms are used to link the molecule with Au atoms, which can be act as electrodes for applying electric field.

Computational details

The Au and S substituted DVCH molecule has been optimized for the zero and the applied field of four biasing steps (0.05,

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0.10, 0.15 and 0.21 $\text{V}\text{\AA}^{-1}$) by high level DFT method using Gaussian09 program package (Frisch *et al.*, 2009). The whole calculation is performed by using a combination of Becke's three-parameter exchange function with non-local correlation of Lee, Yang and Parr (B3LYP hybrid function) with LANL2DZ basis set, as it provides the detailed description of heavy metal atoms in the molecule (Becke, 1993 and Ramirez-Solis *et al.*, 2008). All the geometry optimizations were performed via Berny algorithm with the threshold of 0.00045, 0.0003, 0.0018 and 0.0012au for the maximum force, root mean square force (RMS), maximum displacement and RMS displacement respectively. Here, we have performed all these quantum chemical calculations for various levels of applied EFs to study the changes in structural and the electrostatic properties of the molecule. The HOMO-LUMO isosurface maps and energy level graph of the molecule have been plotted using GVIEW (Frisch *et al.*, 2009). The GaussSum program (Boyle, 2008) has been used to plot the density of states (DOS) spectrum of the molecule for various applied EFs.

RESULTS AND DISCUSSION

Structural aspects

The geometric parameters particularly bond length is a significant parameter for adjusting the electrical properties of conducting molecules (Selvaraju *et al.*, 2012). Also, the average difference between the adjacent single and double bonds known as the bond length alternation along the backbone of a conjugated system plays a vital role for tuning the transport properties. Therefore, a detailed study of bond length variation under the EF interaction is instructive for understanding the relationship between molecular structure and property. The optimized geometry of Au and S substituted molecule for the zero and the maximum applied EF ($0.21 \text{ V}\text{\AA}^{-1}$) are illustrated in Fig. 2. The thiol atom forms an excellent link (Alexei V. Tivanski *et al.*, 2005) between the molecule and the Au atom.

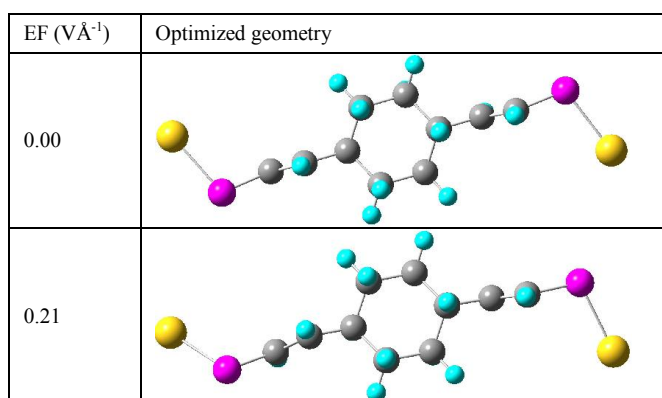


Fig. 2. Optimized geometry of DVCH molecule for the zero and maximum applied EF ($0.21 \text{ V}\text{\AA}^{-1}$)

The C–C bond distances in the aromatic ring in the molecule vary from 1.545 to 1.558 \AA for various applied EFs. For the zero field, the C–C double bond distances of the molecule linked to thiol atoms S(1) and S(2) are the same (1.353 \AA). Increasing the applied fields, the C–C double bond distance linked to S(1) slightly decreases, whereas, the same C–C double bond distance linked to S(2) increases. However, the

zero field bond distances of all the C–H bonds in the molecule almost remain same ($\sim 1.102 \text{\AA}$) for various applied fields. The zero field distance of S–C bonds in the either end of the molecule is $\sim 1.829 \text{\AA}$; as the field increases, slight variation (0.001 \AA) is observed in the L-end. However, the variation in the R-end is greater (0.005 \AA) than the L-end. As the field increases, the distance of Au–S bonds in the L-end decreases from 2.398 to 2.395 \AA , while in the R-end, the distance increases from 2.399 to 2.409 \AA ; however, the variations in both ends are unequal. And, for the maximum applied field ($0.21 \text{ V}\text{\AA}^{-1}$) the variations at L- and R-ends are 0.003 and 0.010 \AA respectively. The calculated values of the bond distances from this study are very close to the previously reported values (Srinivasan *et al.*, 2009 and David Stephen *et al.*, 2011). Even though almost all the bond distances varied by the application of external field, specifically, the S–C and Au–S bonds have uniform and systematic variation. Fig. 3 Shows the variation of bond lengths for various applied EFs with reference to zero field. The bond lengths of Au and S substituted DVCH for various applied EFs are presented in Table 1.

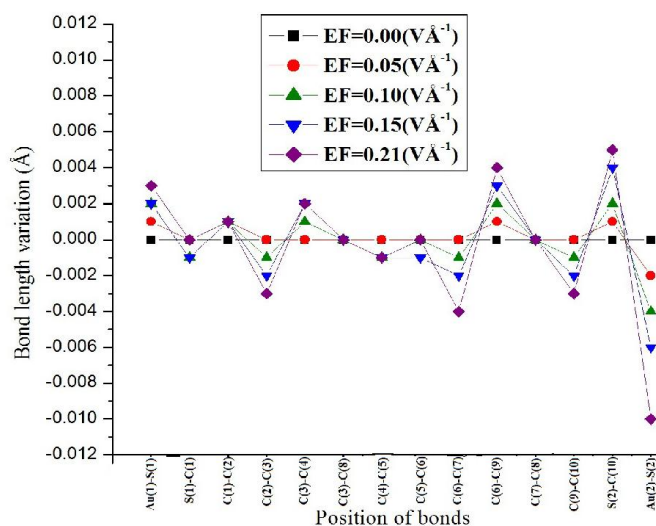


Fig. 3. Variation of bond lengths for various applied EFs with reference to zero field

Table 1. Bond lengths (\AA) of the Au and S substituted DVCH molecule for the zero and various applied EFs

Bonds	Applied electric field				
	0.00	0.05	0.10	0.15	0.21
C(1)-C(2)	1.353	1.352	1.352	1.352	1.352
C(2)-C(3)	1.512	1.512	1.513	1.514	1.515
C(3)-C(4)	1.555	1.555	1.554	1.553	1.553
C(3)-C(8)	1.555	1.555	1.555	1.555	1.555
C(4)-C(5)	1.545	1.545	1.546	1.546	1.546
C(5)-C(6)	1.555	1.555	1.555	1.556	1.555
C(6)-C(7)	1.556	1.556	1.557	1.558	1.56
C(6)-C(9)	1.512	1.511	1.510	1.509	1.508
C(7)-C(8)	1.545	1.545	1.545	1.545	1.545
C(9)-C(10)	1.353	1.353	1.354	1.355	1.356
C(3)-H(3)	1.102	1.102	1.102	1.102	1.102
S(1)-C(1)	1.829	1.829	1.830	1.830	1.830
S(2)-C(10)	1.830	1.829	1.828	1.826	1.825
Au(1)-S(1)	2.398	2.397	2.396	2.396	2.395
Au(2)-S(2)	2.399	2.401	2.403	2.405	2.409

Atomic charges

Nowadays, numerous theoretical methods are used to determine the atomic charges of the molecules by using

quantum chemical calculations. The most frequently used are Natural population analysis (NPA), Mulliken population analysis (MPA), Chelpg scheme and Merz-kollman (MK) schemes (Mulliken, 1955; Singh and Kollman 1984 and Martin and Zipse, 2005). In the present study, the atomic charges of the Au and S substituted DVCH molecule have been analyzed from the charges obtained by MPA and NPA methods. The MPA charges of all C-atoms possess negative charge and vary with the increase of field, the maximum observed variation is 0.035e. The MPA charges of all H-atoms for the zero field are $\sim 0.188e$ and vary slightly for the increase of field. The linker S(1) atom possess positive MPA charge for zero field (0.056e), which slightly decreases with increase of field (0.046e), whereas, the charge of S(2) atom increases to 0.059e. As the field increases, the charges of Au atom at L-end slightly increase from -0.06 to 0.017e, but the same at the R-end varies from -0.061 to -0.13e. The variations of MPA charges for various EFs with reference to zero field are shown in Fig 4. Table 2 displays the MPA atomic charges (e) of the molecule for various applied EFs ($\text{V}\text{\AA}^{-1}$).

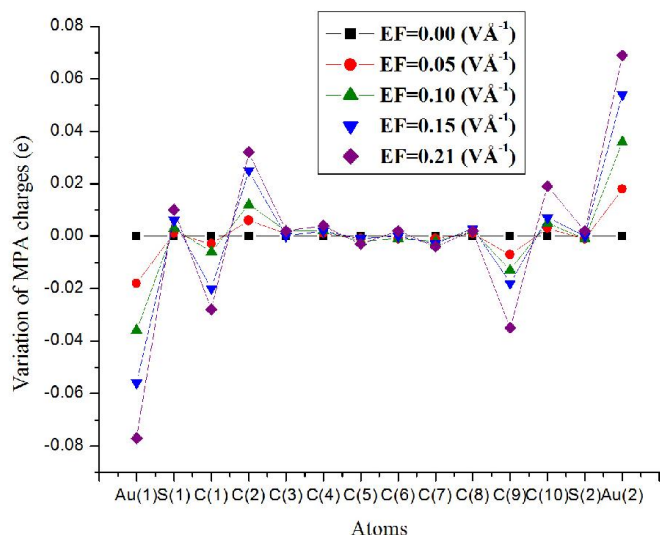


Fig. 4. Variation of MPA charges of the molecule for the zero and various applied EFs

Table 2. MPA atomic charges (e) of the molecule for various applied EFs ($\text{V}\text{\AA}^{-1}$)

Atoms	Applied electric field				
	0.00	0.05	0.10	0.15	0.21
C(1)	-0.549	-0.546	-0.543	-0.529	-0.521
C(2)	-0.025	-0.031	-0.037	-0.050	-0.057
C(3)	-0.038	-0.039	-0.040	-0.038	-0.040
C(4)	-0.423	-0.424	-0.425	-0.425	-0.427
C(5)	-0.425	-0.424	-0.423	-0.424	-0.422
C(6)	-0.038	-0.037	-0.037	-0.038	-0.040
C(7)	-0.422	-0.421	-0.420	-0.419	-0.418
C(8)	-0.424	-0.425	-0.426	-0.427	-0.426
C(9)	-0.021	-0.014	-0.008	-0.003	0.014
C(10)	-0.555	-0.558	-0.560	-0.562	-0.574
H(3)	0.188	0.188	0.189	0.188	0.188
S(1)	0.056	0.055	0.053	0.050	0.046
S(2)	0.056	0.059	0.059	0.058	0.059
Au(1)	-0.060	-0.042	-0.024	-0.004	0.017
Au(2)	-0.061	-0.079	-0.097	-0.115	-0.130

For the zero field, the NPA charge for all C-atoms are found almost negative, and the H-atoms are positive; when the field

increases, the charges of the atoms are found almost increases. For the zero field, the NPA charges of all H-atoms are $\sim 0.213e$ and almost remains same for the increase of field. As the field increases, the NPA charge of S-atom at the L-end decreases gradually from -0.148 to -0.166e, while at the R-end the zero field charge (-0.149e) increases to -0.134e. As the field increases, the charge of Au(1) atom increases from 0.189 to 0.274e, but the same for Au(2), the effect is opposite ie the value decreases from 0.188 to 0.112e (Table 3). The variation of NPA charges for various applied EFs with reference to zero field are shown in Fig 5. On the whole the linker thiol atoms and Au electrodes exhibit uniform and systematic variation for the increase of field.

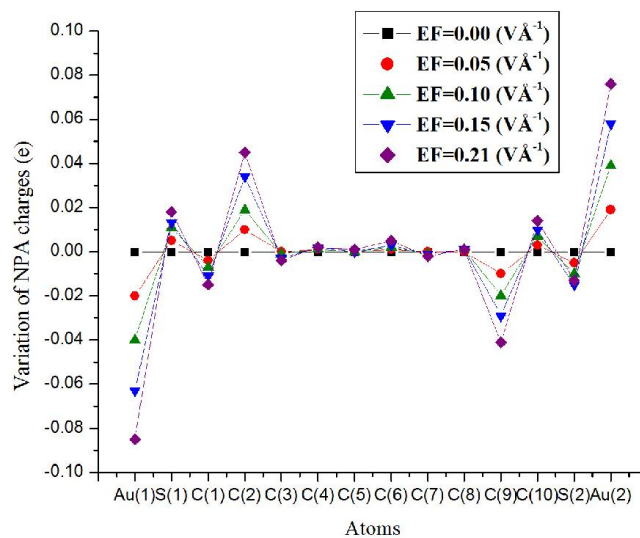


Fig. 5. Variation of NPA charges of the molecule for the zero and various applied EFs

Table 3. NPA atomic charges (e) of the molecule for various applied EFs ($\text{V}\text{\AA}^{-1}$)

Atoms	Applied electric field				
	0.00	0.05	0.10	0.15	0.21
C(1)	-0.346	-0.342	-0.339	-0.335	-0.331
C(2)	-0.160	-0.170	-0.179	-0.194	-0.205
C(3)	-0.236	-0.236	-0.235	-0.233	-0.232
C(4)	-0.408	-0.409	-0.409	-0.41	-0.410
C(5)	-0.408	-0.408	-0.408	-0.408	-0.409
C(6)	-0.237	-0.238	-0.239	-0.24	-0.242
C(7)	-0.408	-0.408	-0.407	-0.407	-0.406
C(8)	-0.408	-0.408	-0.409	-0.409	-0.409
C(9)	-0.158	-0.148	-0.138	-0.129	-0.117
C(10)	-0.347	-0.350	-0.354	-0.357	-0.361
H(3)	0.213	0.213	0.213	0.213	0.212
S(1)	-0.148	-0.153	-0.159	-0.161	-0.166
S(2)	-0.149	-0.144	-0.139	-0.134	-0.136
Au(1)	0.189	0.209	0.229	0.252	0.274
Au(2)	0.188	0.169	0.149	0.13	0.112

Molecular orbital analysis

Generally, for any molecular level device, the charge transport characteristics are mainly controlled by the nature of the molecular orbitals. The spatial distribution and the energy level of a molecular orbital (MO) determine its contribution to the conductivity (Csizmadia, 1976 and Leach, 2001). The charge transfer through a particular MO gradually decreases as we go away from the Fermi level of the electrode. Further, the MOs, which are fully delocalized, contribute more to conduction channel (Leach, 2001 and Lu *et al.*, 2004). The

frontier molecular orbitals are the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and the difference between them is known as HOMO-LUMO gap (HLG). The charge transport properties of the molecule (Lu *et al.*, 2004 and Ashkan shafiee, 2011) are determined by the difference of energy between HOMO and LUMO. Hence, it is essential to examine the variations of HLG and molecular orbital energy levels of the molecule for the various applied EFs. Fig. 6 shows the spatial redistribution of molecular orbital of Au and S substituted DVCH for various applied EFs. The applied EF partially localizes the frontier orbitals (HOMO and LUMO) of the molecules, which are opposite to each other, this can be well understood from the Fig. 6. The Fig. 7 shows the energy level diagram of Au and S substituted DVCH molecule for the zero and various applied EFs.

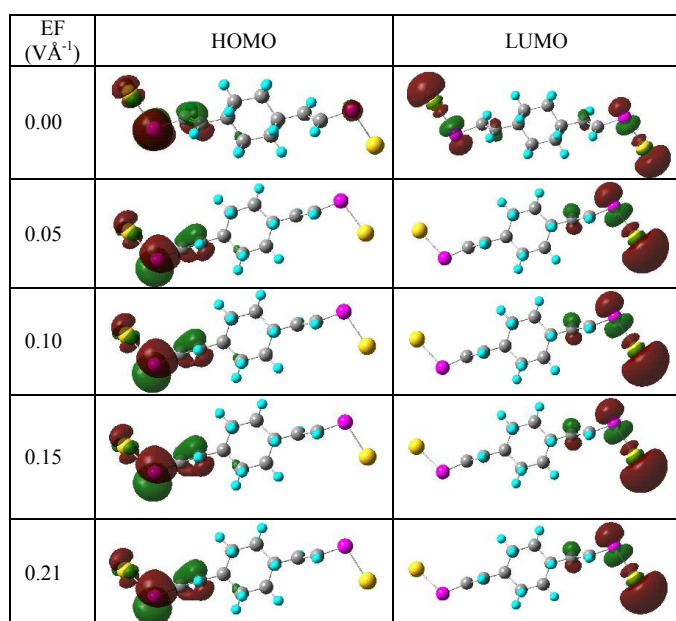


Fig. 6. Isosurface representation of molecular orbitals of Au and S substituted DVCH molecule for the zero and various applied EFs, which are drawn at 0.02 au surface values

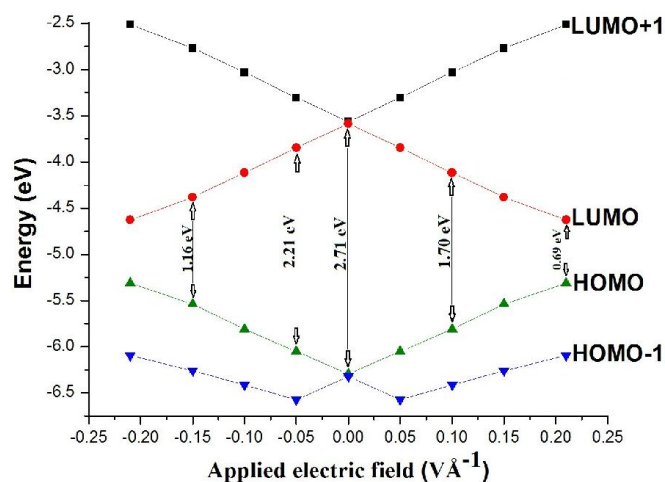
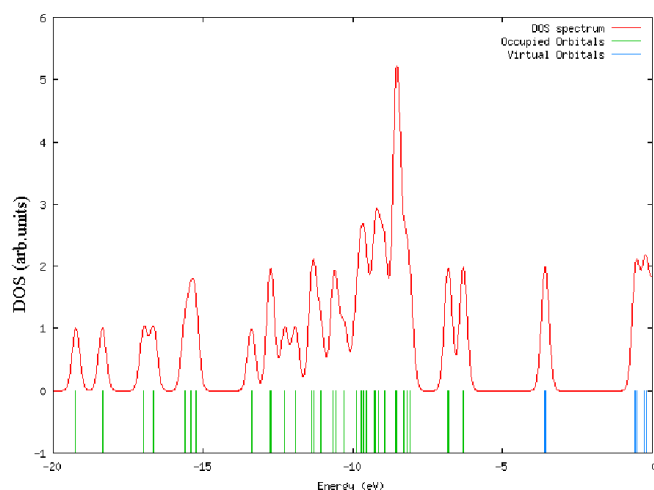


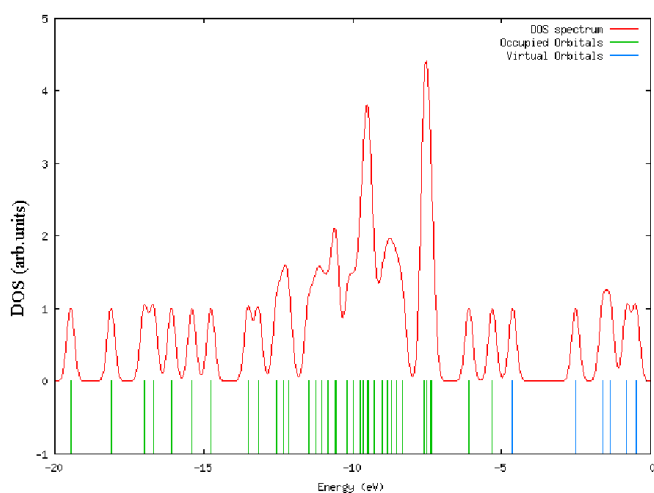
Fig. 7. Energy level diagram of Au and S substituted DVCH molecule for the zero and various applied EFs

For the applied field (0 - 0.21 $\text{V}\text{\AA}^{-1}$), the HLG decreases from 2.71 to 0.69 eV. This variation is also confirmed from the

spectrum of density of states (DOS). Fig.8 [(a) & (b)] shows the DOS of Au substituted molecule for zero field and 0.21 $\text{V}\text{\AA}^{-1}$, in which, green lines represent the HOMO and blue lines represent the LUMO. Notably, the presence of gold atoms in the molecule broadens the DOS peaks with the decrease of HLG. However, from Fig. 6 it is clear that all the atoms of DVCH molecule between the two terminal thiol atoms are not delocalized completely. Hence, even though small HLG exists in this molecular system, the possibility of conduction through the molecule is found to be very less, therefore, it almost acts as an insulator.



(a) $\text{EF}=0.00 \text{ V}\text{\AA}^{-1}$



(b) $\text{EF}=0.21 \text{ V}\text{\AA}^{-1}$

Fig. 8. DOS spectrum of Au and S substituted DVCH for (a) zero and (b) maximum applied field

Molecular dipole moment

When the molecule is subjected to an external EF, the delocalization of π - electron of the conjugated organic molecules lead to redistribution of charges of the molecular chain, consequently, the dipole moment of the molecule changes (Freude, 2005). Hence, we can roughly estimate the ability of electron transport by simply comparing the dipole moments of the molecule for various applied EFs. The variations of molecular dipole moment for the various applied EFs were analyzed by several researchers (Mazurkiewicz and Tomasiak, 2012 and Kirtman *et al.*, 2002) and found a linear

character. Here, we have calculated the dipole moment of the molecule for zero as well as various applied EFs. The resultant molecular dipole moment (μ_T) for zero bias is 0.21 D, which increases almost linearly with the increase of field.

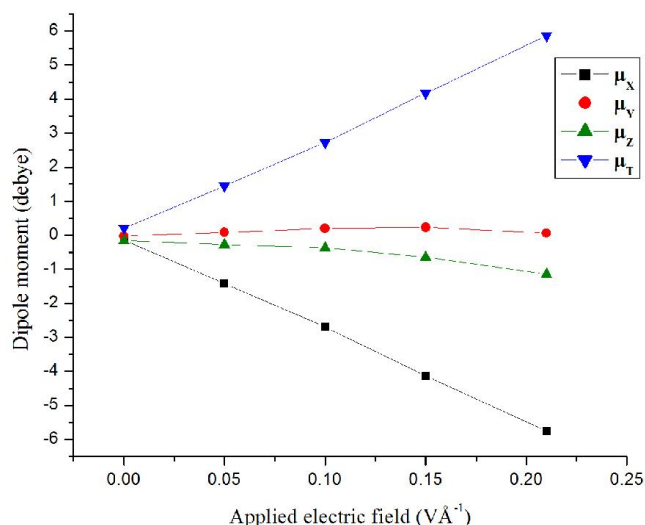


Fig. 9. Molecular dipole moment of Au and S substituted DVCH molecule for the zero and various applied EFs

However, the polarization effect on the molecule is small for the increase of field, and the dipole moment becomes 5.86 D for the maximum applied field (0.21 VÅ⁻¹). Fig. 9 shows the variation of x, y and z components of dipole moment (μ_x , μ_y , and μ_z) and the resultant molecular dipole moment (μ_T) for various applied EFs, the large variation of x-component may be due to the application of field along x-direction.

Conclusion

The present theoretical density functional study on Au and S substituted 1,4-divinylcyclohexene molecule describes the structural variations and the electrical characteristics for zero and various external applied fields. A systematic and almost uniform variation has been observed for the terminal bonds of the molecule for various applied EFs. When the field increases, the hybridization of molecular levels broaden the DOS and decreases the HOMO-LUMO gap from 2.71 eV to 0.69 eV. From the isosurface representation of molecular orbitals, it is clear that all the atoms of DVCH molecule between the two terminal thiol atoms are not delocalized. Hence, even though small HLG exists in this molecular system, the possibility of conduction through the molecule is found to be very less, therefore, it almost acts as an insulator. Further, the applied field does not polarize the molecule significantly, hence, the dipole moment of the molecule increases slightly from 0.21 to 5.86 D. The study of structural properties of the molecule gives an idea to tune this kind of insulating molecules for appropriate biasing voltages for the operation of molecular devices; further, this study may be useful to synthesize insulating layers.

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