First-principles study of Trans-Polyacetylene

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ABSTRACT

First-principles calculations based on Density Functional Theory has been employed to simulate the structure of Trans-Polyacetylene with two monomers per unit cell and also with four monomers per unit cell. Structural parameters have been measured. Electron density of states, dielectric constant and phonon modes have been computed in both cases and the results have been reported in the present paper. Calculation of the electronic component of dielectric constant along different directions indicates that the conformation having four monomers per unit cell is not that stable as compared to the conformation with two monomers per unit cell.

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INTRODUCTION

Conducting polymers have emerged as a new technologically important potential class of materials which has attracted scientific community to a larger extent[1]. They are fundamentally different from other conventional inorganic semiconductors essentially because, these materials have highly anisotropic quasi-one dimensional structure. They have a chain-like structure which leads to strong coupling of the electronic states to conformational excitations. Also, they will be having relatively weak inter-chain binding which allows diffusion of dopant molecules into the structure[2]. But the strong intra-chain carbon – carbon bonds will maintain the integrity of the polymer.

Polyacetylene is the simplest among the conjugated polymers. It is an organic polymer with the repeating unit $(C2H2)_n$. It will be consisting of weakly coupled chains of CH units. The discovery of the high conductivity of polyacetylene by Hideki Shirakawa, Alan J.

Heeger, and Alan G MacDiarmid got the Nobel Prize in Chemistry in 2000[3]. Polyacetylene has been considered as the prototype example for the conducting polymers. Thus, study of this polymer has attracted a larger scientific community. This polymer consists of a long chain of carbon atoms with alternating single and double bonds between them, each with one hydrogen atom. It has got mainly two conformations – cis and the trans.

Any little modification in the structure and composition of a Polymer will bring in sufficient changes in the properties of the polymer[4,5]. Thus it is important to study the structure of the Polymers and look at the parameters which can be altered to get a better material for technological applications. First-principles calculations based on Density Functional Theory[6] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of polymers[7,8]. With this in view, structure of trans-Polyacetylene has been simulated using First-principles calculations based on

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Density Functional Theory in two conformations – that is with two molecules per unit cell [PA2] and four molecules per unit cell [PA4]. Computations of Electronic density of states, Dielectric constant and phonon modes have been done and the results have been reported in the present paper.

COMPUTATIONAL DETAILS

Several codes are available for the theoretical structure simulation[9]. We use plane wave self consistent field (PWSCF)[10] implementation of density functional theory (DFT), with a Local density approximation (LDA)[11] to exchange correlation energy of electrons and ultrasoft pseudopotentials[12], to represent interaction between ionic cores and valence electrons. Kohn-Sham wave functions were represented with a plane wave basis with an energy cutoff of 40 Ry and charge density cutoff of 240 Ry. Integration over Brillouin zone was sampled with a Monkhorst-Pack scheme[13] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme[14] with broadening of 0.003 Ry. The structure was relaxed to minimize energy.

RESULTS AND DISCUSSION

Structure of PA2 and PA4

The structure was first stimulated using Avagadro[15] and then the coordinates were fed into pwscf input file. The structure has been optimized using energy minimization technique. Completely relaxed structure of the Polyacetylene was observed using the XCrySDen software[16] and the structures as seen along a random direction have been given in Figures 1 and 2.

B.S. Good et. al.[17] have carried out investigation of the structure of Polyacetylene at low temperatures taking into account of intra-chain interactions and have found that the most stable configuration at low temperature appears to be the cis-transoid conformation. J. W. Mintmire and C.T. White have applied Xα approach for the determination of electronic and geometric structure of Polyacetylene[18]. D.S. Suh et. al.[19] have studied the helical Polyacetylene heavily doped with iodine. Studies have also been carried out on Polyeth-

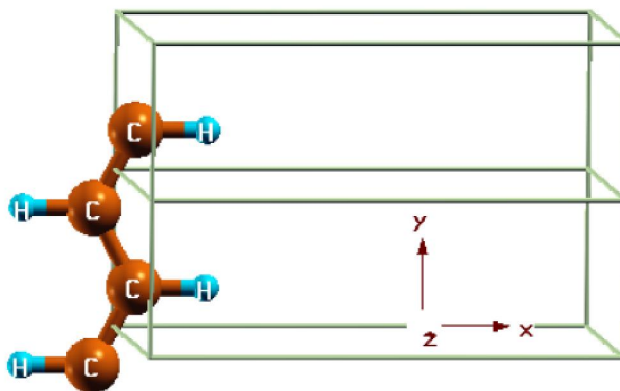ylene/Polyacetylene composites to look at the improvement in the conducting properties[20].

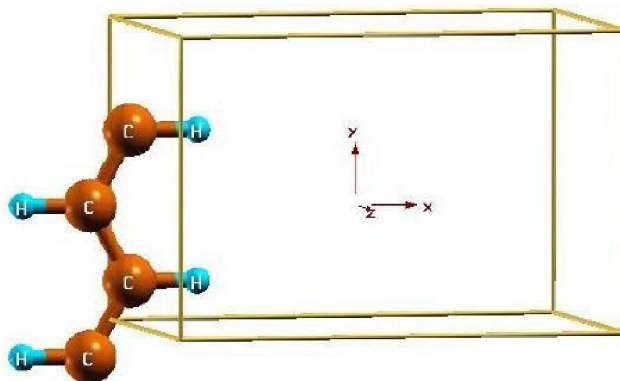**Figure 1 : Structure of PA2 as viewed along a random direction**

Figure 2 : Structure of PA4 as viewed along a random direction

Structural parameters of the simulated structural patterns of PA2 and PA4 are given in TABLES 1, 2 and 3.

TABLE 1 : Bond lengths in PA2 and PA4

Bond	Bond length (Å) in PA2	Bond length (Å) in PA4
C – C	1.3708	1.375
H – C	1.0991	1.098

TABLE 2 : Bond angles in PA2 and PA4

	Bond angle (deg) in PA2	Bond angle (deg) in PA4
C – C – H	117.59	118.16, 118.03
C – C – C	124.8	123.81

TABLE 3 : Other parameters in PA2 and PA4

Parameter	PA2	PA4
a	7.36 Å	7.36 Å
b	2.43 Å	4.86 Å
c	4.78 Å	4.78 Å
Unit cell	Orthorhombic	Orthorhombic

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EDOS calculation

Electron Density of States (EDOS) have been computed in PA2 and PA4 using Electronic structure calculation code of Quantum espresso and the same are shown in Figures 3 and 4. The material shows a band gap of 2.19 and 2.15 respectively in PA2 and PA4 conformations.
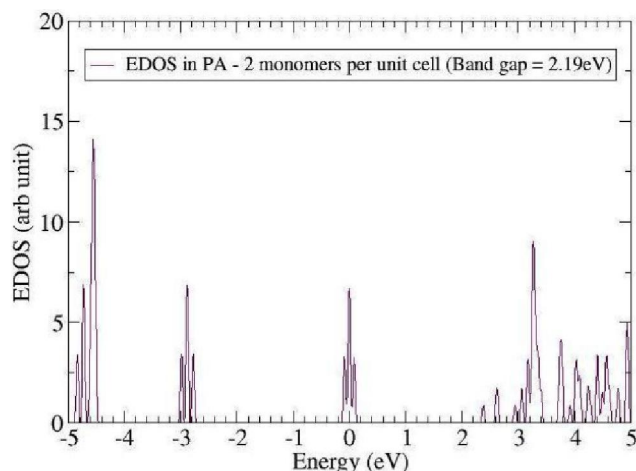

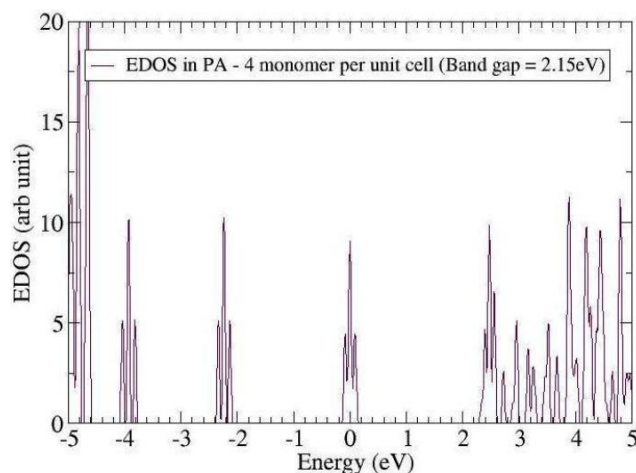**Figure 3 : Electron density of states in PA2**

Figure 4 : Electron density of states in PA4

Phonon modes and dielectric constant

The computed phonon modes at the gamma point range from $124cm^{-1}$ to $3022cm^{-1}$ in case of PA2 and $11cm^{-1}$ to $3037cm^{-1}$ in case of PA4. Dielectric constant of the polymer in two conformations PA2 and PA4 have been computed. In case of PA2, it comes out to be 1.446, 1.511 and 1.303 along X, Y and Z axes respectively and the average value comes out to be 1.42. Dielectric constant in case of PA4 comes out to be 1.47 along X axis. But it shows impracticable values (289757

and -1.164) along Y and Z axes. Thus, among these two conformations PA2 is highly stable than the conformation PA4.

CONCLUSIONS

First-principles calculations based on DFT has simulated the structure of trans-Polyacetylene in two conformations PA2 and PA4. EDOS calculations show that the polymer has a band gap of 2.19eV and 2.15eV in case of PA2 and PA4 respectively. Phonon modes range from $124cm^{-1}$ to $3022cm^{-1}$ in case of PA2 and $11cm^{-1}$ to $3037cm^{-1}$ in case of PA4. Calculations of the dielectric constant show that among the two simulated structures PA2 is more stable than PA4.

ACKNOWLEDGEMENTS

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