

First-Principles Study of Dielectric Constant and Polarizability in Polydiacetylene Crystal

H. S. Omkar¹ and H. R. Sreepad²

¹Department of Mechanical Engineering, RajaRajeswari College of Engineering,
Kumbalagodu, Bengaluru, Karnataka, India

²P. G. Department of Physics, Government College (Autonomous),
Mandya, Karnataka, India
E-Mail: hrsreepad@gmail.com

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Abstract - First principles calculations based on Density Functional Theory have been done on Polydiacetylene. Its triclinic unit cell has been simulated. Band gap in case of this material comes out to be 0.75eV. This value is in the range exhibited by semiconducting materials. Dielectric constant and Polarizability of the material have been computed. The value of dielectric constant comes out to be 50.6, 59.6 and 44.6 along X, Y and Z axes respectively and its average value comes out to be 51.6. Polarizability comes out to be 33.7 (Å)³, 34 (Å)³ and 33.4 (Å)³ along X, Y and Z axes respectively with an average value of 33.7 (Å)³.

Keywords: Polydiacetylene, Dielectric Constant, Electronic Density of States, First-principles Calculations, Polarizability, Chemical Engineering

I. INTRODUCTION

Polydiacetylene (PDA) is a unique, essentially one-dimensional, fully conjugated polymer. It can be polymerized without disruption of the crystallinity of its monomer. Because of its high degree of ordering, the backbone structure of PDA provides an attractive conjugated system for the transport studies. Pristine PDA crystals show high value of charge carrier mobility. The charge transport in polydiacetylene quasi-1D single crystals (PDA-PTS) has been studied as a function of temperature, electric and magnetic fields by Aleshin *et.al.*, [1]. G. Weiser *et.al.*, [2] have measured Electric-field-modulated reflectivity of three different polydiacetylenes - PTS, poly[2,4-hexadiyne-1,6-diol-bis(p-toluene sulfonate)]; PFBS, poly[2,4-hexadiyne-1,6-diol-bis(p-fluorobenzene sulfonate)]; and DCHD, poly[1,6-di(n-carbazolyl)-2,4-hexadiyne] - and is analyzed with respect to the underlying mechanism for the observed sensitivity of π - π^* transitions to electric fields. PDA crystals are expected to show non linear optical properties [3]. The relationship between structure and mechanical properties of polydiacetylene single-crystal fibers has been studied in detail by Galiotis *et.al.*, [4].

It has been found that any little modification in the structure and composition of a material will bring in sufficient changes in the properties of the material [5, 6]. Thus it is important to study the structure of the materials and look at the parameters which can be altered to get a better material for technological applications. First-principles calculation

based on Density Functional Theory [7] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of organic materials [8, 9]. Polydiacetylene crystals have attracted the scientific community in various aspects [10 – 12]. With this in view, structure of a Polydiacetylene crystal C₁₅H₁₂N₃ has been simulated using First-principles calculations based on Density Functional Theory and computation of Electronic density of states, Dielectric constant and Polarizability have been done and the results have been reported in the present paper.

II. COMPUTATIONAL DETAILS

Several codes are available for the theoretical structure simulation [13]. The density functional theory approach has emerged as a well established computational method. It has been widely employed to arrive at the conformations of a large number of molecular systems. The practical applicability and sophistication of DFT is strongly sensitive to the good choice of exchange–correlation function along with the appropriate basis set.

Quantum espresso is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modelling. It is based on density-functional theory, plane waves, and pseudopotentials. Author has used plane wave self consistent field (PWSCF) [14] implementation of density functional theory (DFT), with a Local density approximation (LDA) [15] to exchange correlation energy of electrons and ultrasoft pseudopotentials [16], 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 30 Ry and charge density cutoff of 180 Ry. Integration over Brillouin zone was sampled with a Monkhorst-Pack scheme [17] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme [18] with broadening of 0.03 Ry. The structure was relaxed to minimize energy.

III. RESULTS AND DISCUSSION

In the present study, the Triclinic unit cell of Polydiacetylene was first simulated using “Avogadro” [19]. Later, atomic positions of the simulated structure have been used in the plane wave self-consistent field calculations. The structure was relaxed and the optimized values of the unit cell parameters thus arrived at through minimization of energy are; $a=3.894 \text{ \AA}$, $b=7.619 \text{ \AA}$, $c=5.159 \text{ \AA}$, $\alpha=80.2^\circ$, $\beta=96.6^\circ$ and $\gamma=91.5^\circ$. “scf” calculation was done using the final atomic positions obtained after relaxing the structure using the program 'pw.x' of Quantum espresso.

Completely relaxed structure of the unit cell was visualized using the program “XcrysDen”[20] and the structure of unit cell of Polydiacetylene as seen along X-axis and Z-axis are shown in Figures 1 and 2 respectively. James L. Foley et. al.,[10] have carried out X-ray diffraction study in a Polydiacetylene single crystal and have reported a triclinic structure with unit cell parameters; $a=4.9052 \pm 0.0003 \text{ \AA}$, $b=10.921 \pm 0.001 \text{ \AA}$, $c=11.833 \pm 0.002 \text{ \AA}$, $\alpha=87.908 \pm 0.011^\circ$, $\beta=86.45 \pm 0.01^\circ$ and $\gamma=83.132 \pm 0.007^\circ$. The simulated crystal in the present study looks to be different from this material.

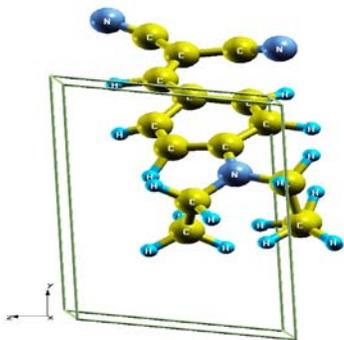


Fig. 1 Structure of unit cell of Polydiacetylene Crystal as seen along X-axis

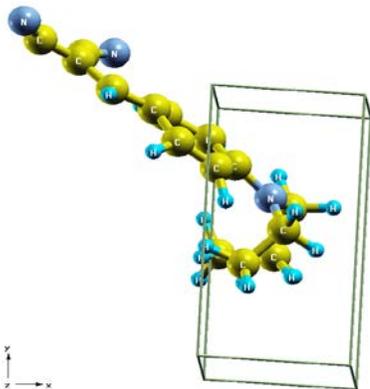


Fig. 2 Structure of unit cell of Polydiacetylene Crystal as seen along Z-axis

A. EDOS Calculation

Electron Density of States (EDOS) has been computed in Polydiacetylene using Electronic structure calculation code

of Quantum espresso. EDOS in Polydiacetylene has been shown in Figure 3. As it can be seen from the figure 3, the material shows semiconducting nature with a band gap of 0.75 eV.

Band gap in case of Azobenzene has been found to be 0.67eV [21]. A Band gap of 0.74eV has been observed in case of 4-Chloro-Phenyl-Benzamide [22]. Gallium arsenide shows a band gap of 1.43eV and Germanium shows a band gap of 0.67eV. Indium nitride, Gallium antimonide and Gallium arsenide antimonide show the band gap of 0.7eV, 0.726 and 0.7 respectively [23,24].

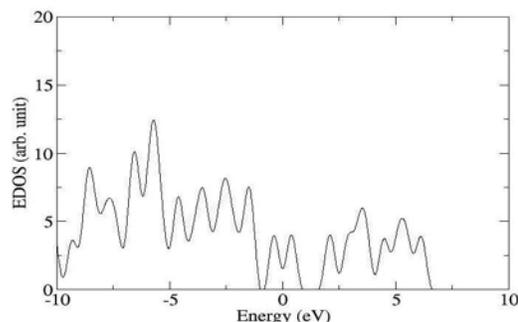


Fig. 3: Electron Density of States in Polydiacetylene Crystal

B. Dielectric Constant and Polarizability

Dielectric constant has been computed in case of Polydiacetylene. The value of dielectric constant in Polydiacetylene comes out to be 50.6, 59.6 and 44.6 along X, Y and Z axes respectively and its average value comes out to be 51.6. Polarizability of Polydiacetylene has also been estimated and it comes out to be $33.7 (\text{\AA})^3$, $34 (\text{\AA})^3$ and $33.4 (\text{\AA})^3$ along X, Y and Z axes respectively with an average value of $33.7 (\text{\AA})^3$.

IV. CONCLUSIONS

The simulated and optimized structure of Polydiacetylene is different from the one studied by X-ray diffraction. The EDOS calculation shows that the material shows semiconducting nature with a band gap of 0.75 eV. The material shows dielectric constant values 50.6, 59.6 and 44.6 along X, Y and Z axes respectively and its average value comes out to be 51.6. The polarizability values are found to be $33.7 (\text{\AA})^3$, $34 (\text{\AA})^3$ and $33.4 (\text{\AA})^3$ along X, Y and Z axes respectively with an average value of $33.7 (\text{\AA})^3$.

V. ACKNOWLEDGMENTS

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