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FLUORINATION OF POLYFORMALDEHYDE: STRUCTURAL PATTERN RECOGNITION STUDY USING FIRST-PRINCIPLES

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Abstract- Fluorination of organic compounds is an important task which brings in changes in Physical and Chemical parameters in the organic material. Even the structural pattern of the molecule gets altered due to replacement of Hydrogen atoms by Fluorine atoms. Structural pattern recognition in case of molecules is an important task in the field of bio-engineering. Theoretical structure simulation is also employed in this technologically important field. An attempt has been made to look for the changes that take place due to fluorination in the technologically important polymer Polyformaldehyde. Electronic Density of States and Phonon modes in the material have been computed using First-principles calculations based on Density Functional Theory.

Key words - Electron Density of States, First-principles, Phonons, Structural Pattern recognition, Theoretical structure simulation, Density Functional Theory, Fluorination, Polyformaldehyde.

Introduction

Structural pattern recognition study plays an important role in the world of molecules. Several experimental techniques indirectly work on the basis of pattern recognition by looking at the signatures of molecules [1-3].

Bio-engineering highly depends on the structural pattern recognition of bio-molecules. Some of the available prominent experimental techniques are X-ray image plating, Fourier Infra-Red Spectroscopy and Raman Spectroscopy [4-6].

Theoretically also, one can look for structural pattern recognition in organic molecules. Structure simulation is one such technique which is widely used in this field. Fluorination of organic compounds is an important task. Because, it can bring in several changes in physical and chemical properties of molecules [7,8].

Structure Simulation

Structure simulation can be done using several programs [9]. Using those codes one can simulate different possible structures for a given molecule. Theoretically one can look at various parameters of the simulated structures.

Using those parameters one can compute several other physical and chemical parameters pertaining to those structures. By looking at the computed values, one can decide whether the structure is feasible or not. Hence one can arrive at a definite conclusion regarding the possible structure without any ambiguity. Phonon modes calculated at the gamma point and along different axes give a clear idea about the stability of the structural pattern of the simulated molecule.

Computational Details

First-principles calculations based on Density Functional Theory (DFT) can be effectively used to study the internal structure and properties of the material in detail [10].

We use plane wave self consistent field (PWSCF) [11] implementation of density functional theory (DFT), with a Local density approximation (LDA) [12] to exchange correlation energy of electrons and ultrasoft pseudopotentials [13], 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 [14] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme [15] with broadening of 0.003 Ry. The structure was relaxed to minimize energy.

Material under Study

Polyformaldehyde is a technologically important polymer. Corrosion resistant conductive Polyformaldehyde compositions with carbon nanotube and carbon nano fibre conductive fillers have been patented [16].

Completely relaxed structure of the non fluorinated Polyformaldehyde as observed using the XCrySDen [17] is given in Fig 1. [18].
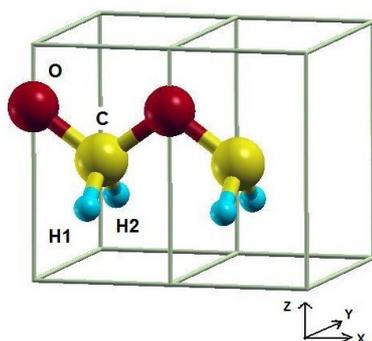
Fig. 1. Structural pattern of non fluorinated Polyformaldehyde

Structural parameters of the simulated structural pattern of Polyformaldehyde are given in Tables I, II and III.

TABLE I
Bond lengths in Polyformaldehyde

Bond	Bond length (Å)
C – O	1.39
C – H	1.12

TABLE II
Bond angles in Polyformaldehyde

Bond	Bond angle (degree)
O – C – O	108
C – O – C	108
H – C – H	107
H – C – O	110

TABLE III
Other Structural Parameters in Polyformaldehyde

Parameter	Value
$H_1 - H_2$ dist	1.79 Å
a	2.25 Å
b	4.11 Å
c	3.78 Å
Vol of unit cell	35 Å^3
Space group	Pmm2; No 25 Orthorhombic

Theoretical structure simulation has been carried out by replacing one Hydrogen atom with Fluorine atom and then by replacing both Hydrogen atoms by Fluorine atoms. The structural parameters of the partially and completely fluorinated Polyformaldehyde are tabulated in Tables IV and V.

TABLE IV
Structural Parameters in partially fluorinated Polyformaldehyde

Parameter	Value
a	2.27 Å
b	4.11 Å
c	3.78 Å
C – F	1.39 Å
C – O	1.39 Å
C – H	1.11 Å
H – F	2.01 Å
O – C – O	110 deg
C – O – C	110 deg
H – C – F	107 deg
F – C – O	108 deg

TABLE V
Structural Parameters in completely fluorinated Polyformaldehyde

Parameter	Value
a	2.3 Å
b	4.8 Å
c	4.0 Å
C – O	1.39 Å
$C - F_1$	1.35 Å
$C - F_2$	1.35 Å
$F_1 - F_2$ dist	2.18 Å
C – O – C	112 deg
$F_1 - C - F_2$	107 deg
$F_1 - C - O$	109 deg
$F_2 - C - O$	109 deg

Electron Density of States (EDOS) have been computed in case of non fluorinated, partially fluorinated and completely fluorinated Polyformaldehyde using Electronic structure calculation code of Quantum espresso and are shown in Figs. 2, 3 and 4.
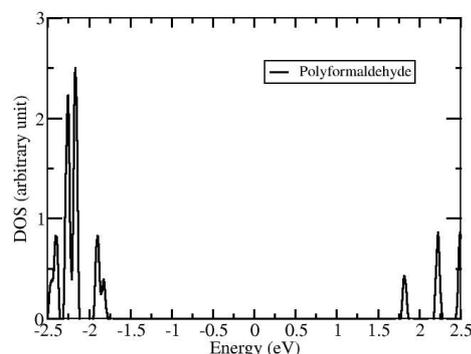

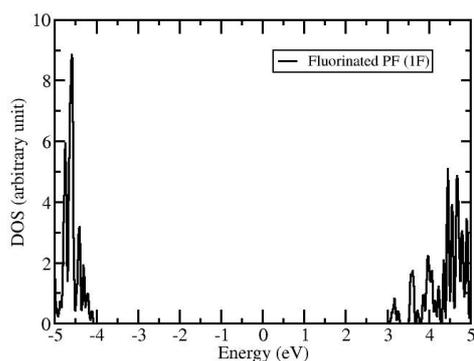Fig. 2. EDOS in non fluorinated Polyformaldehyde
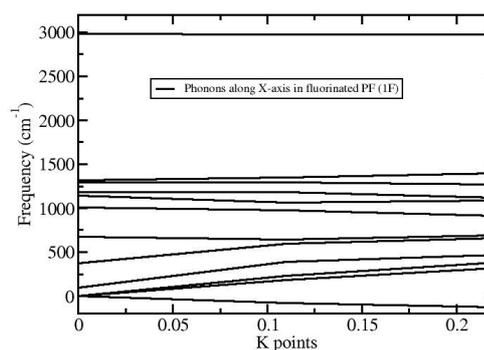
Fig. 3. EDOS in partially fluorinated Polyformaldehyde
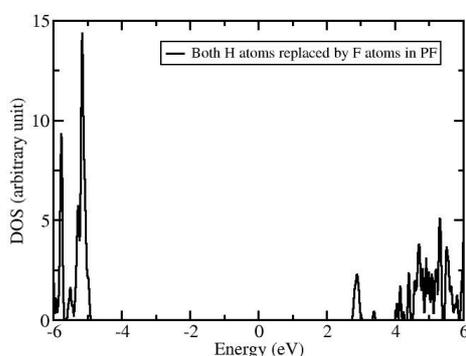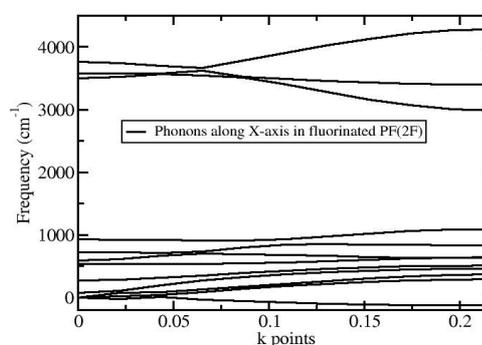

Fig. 4. EDOS in completely fluorinated Polyformaldehyde

The phonon modes along X-axis have been calculated in case of non fluorinated, partially fluorinated and completely fluorinated Polyformaldehyde and are shown in Figs. 5, 6 and 7. Phonon modes indicate that the stability of the molecule decreases due to fluorination. This can be attributed to the deformation caused by replacing Hydrogen atoms by Fluorine atoms having larger radius.
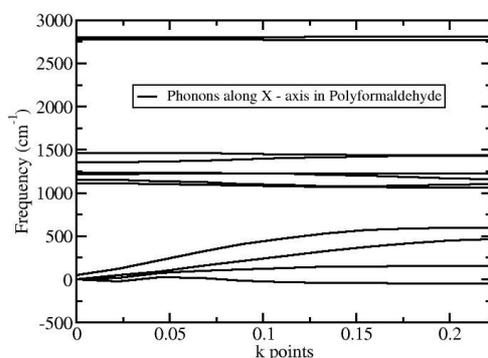

Fig. 5. Phonon modes in non fluorinated Polyformaldehyde

Fig. 6. Phonon modes in partially fluorinated Polyformaldehyde

Fig. 7. Phonon modes in completely fluorinated Polyformaldehyde

Value of Fermi energy and band gap have been obtained from Electron Density of States computation using Electronic structure calculation code of Quantum espresso. The value of Dielectric constant has been computed using the phonon data. The parameters so obtained are tabulated in Tables VI and VII.

TABLE VI
Parameters obtained from EDOS calculations

Sample	Fermi Energy	Bandgap
In non fluorinated PF	2.63 eV	3.51eV
In partially fluorinated PF	4.88 eV	7.07eV
In completely fluorinated PF	4.51eV	7.62eV

TABLE VII
Static Dielectric constant

Sample	Average value
In non fluorinated PF	2.57
In partially fluorinated PF	2.30
In completely fluorinated PF	2.00

As it can be seen from the above tables, the fluorination is bringing change in Electronic Density of States and Phonon modes. It is altering values of Fermi energy,

Band gap and also the value of average static Dielectric constant. The value of band gap increases due to fluorination whereas, the average value of Static Dielectric constant decreases due to fluorination.

Conclusion

Structural pattern recognition plays an important role in deciding the structural conformation of molecules. Fluorination of Polyformaldehyde alters both Electronic Density of States and Phonon modes. The band gap also gets altered. The upper level of frequency in phonon modes increases due to fluorination. This is essentially because of the change in the structural pattern of the molecule due to fluorination.

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