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STRUCTURAL PATTERN RECOGNITION IN MOLECULES

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Abstract- Structural pattern recognition in case of molecules is an important task in the field of bio-engineering. Several techniques are employed in order to get the exact structural conformation and structural parameters of molecules. Present paper discusses some of the available techniques such as Fourier Infra-Red Spectrocopy, Raman Spectroscopy and Theoretical Structure simulation which are employed in this technologically important field. An attempt has been made to look for the exact structural conformation in case of Polyformaldehyde using First-principles calculations based on Density Functional Theory.
Key words - FTIR spectroscopy, Pattern recognition, Raman spectroscopy, Structural parameters, Theoretical structure simulation.

Introduction

Structural pattern recognition is a challenged task in case of several molecules. That too, it is a highly challenged task in case of bio-molecules. Usually, the structure determination is done by employing the well known X-ray diffraction technique. Protein structure determination has been done by several investigators [1,2] using this technique.

But, it has been observed that in several bio-molecules, X-rays themselves bring in changes in the structural pattern. This is because of high sensitivity of those molecules for radiation [3]. It has been observed that irradiation with X-rays and gamma rays cause for radiation induced solid state polymerization in several cyclic oligomers of Formaldehyde [4,5].

X-ray diffraction techniques cannot be used for the study of liquids and gaseous molecules. Several organic compounds which are used for the synthesis of bio-molecules are in liquid form. Thus bio-engineering looks for other techniques which can be employed for structural pattern recognition in case of bio-molecules.

Other techniques for pattern recognition
Fourier Transform Infra-Red Spectroscopy

Fourier Transform Infra-Red Spectroscopy (FTIR) plays an important role in the pattern recognition in case of organic molecules. Digital signatures of the presence of different types of chemical bonds are obtained by looking at the IR frequency modes arising due to different stretching modes of chemical bonds.

FTIR spectroscopy is a measurement technique that allows one to record infrared spectra. Infrared light is guided through an interferometer present in the instrument and then through the sample (or vice versa).

A moving mirror inside the apparatus alters the distribution of infrared light that passes through the interferometer. The signal is recorded directly and is called an 'interferogram'. It represents light output as a function of the mirror position. A data-processing method called 'Fourier transform technique' turns this raw data into the desired result, which comes out as a spectrum with light output as a function of infrared wavelength (or wave number). The sample's spectrum is always compared to a reference [6].
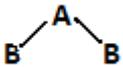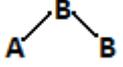
Looking at the wave numbers at which peaks are observed in the spectrum, one gets information about the presence of particular mode of vibration associated with the respective bond.

Raman Spectroscopy

Raman Spectroscopy also plays an important role in the structural pattern recognition of molecules [7]. Polyatomic molecules can be linear or non-linear, symmetric or non-symmetric.

Consider a tri-atomic molecule AB_2. The arrangement of atoms in this case can be any one as listed in Table I

TABLE I
Arrangement of Polyatomic molecules

A – B – B	Linear and non-symmetric
B – A – B	Linear and symmetric
	Non-Linear and symmetric
	Non-Linear and non-symmetric

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For example: CO_2 has Linear and symmetric conformation as shown below:

$$O=C=O$$

116.3 pm
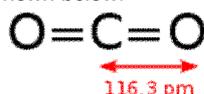
while N_2O has Linear and non-symmetric conformation as shown below:

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$$N\equiv\overset{+}{N}-O^- \longleftrightarrow {}^-N=\overset{+}{N}=O$$

Whereas H_2O has got Non-linear and symmetric conformation as shown below;

95.84 pm
104.45°
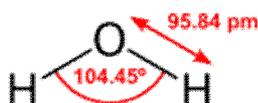
The structural pattern recognition in all the above cases can be done by processing the digital signatures of the respective bonds by looking at the intensity, polarization and frequency of Raman lines [8].

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.

First-principles Study

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].

Computational Details

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].

Polyformaldehyde is generally found to have hexagonal unit cell structure. But Carozzolo & Mammi [17] have discussed a new type of Polyformaldehyde having Orthorhombic unit cell with space group $P2_12_12_1$ and lattice constants a=4.77Å, b=7.65 Å, c=3.56 Å.

It is interesting to see that the single crystals of formaldehyde can be synthesized in the form of cyclic trimer, tetromer, pentomer and hexomers. Hence, understanding of various crystal structures and properties of Polyformaldehyde is important to its technological applications.

Results and Discussion

Different structural conformations have been considered for the Polyformaldehyde [18] (also known as Polyoxymethylene or POM) and phonon modes along X axis have been computed for all the conformations. They are tabulated in Table II.

TABLE II
Simulated Structural Conformations of POM

Conformation	Optical phonon modes (cm)$^{-1}$
1 monomer / u cell – planar (Planar POM)	-1659 to 3139 Unstable
1 monomer / u cell – non planar non-helical (1NPNH) Space group: Pmm2; No 25 – Orthorhombic	54 to 2800 Stable
2 monomers / u cell – non planar non-helical (2 NPNH) Space group: P2; No.3 - Monoclinic	143 to 2830 Unstable
3 monomers / u cell – non planar non-helical (3NPNH) Space group: Pm: No. 6 - Monoclinic	44 to 2985 Unstable
4 monomers / u cell - non planar non helical (4NPNH) Space group: Pmm2: No. 25 - Orthorhombic	93 to 3178 Unstable
4 monomers / u cell – helical (4 Helical) Space group: $P2_12_12_1$ Orthorhomic	55 to 3020 Stable

The respective simulated structures of all the non helical conformations are given below in Figs. 1(a to e):
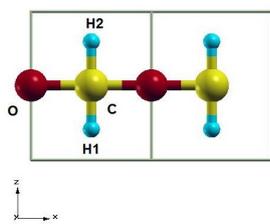
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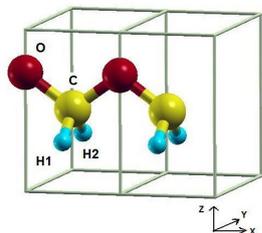Fig. 1(a). Structural pattern of Planar POM
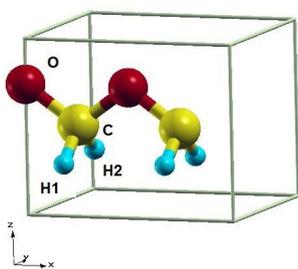

Fig. 1(b). Structural pattern of 1NPNH

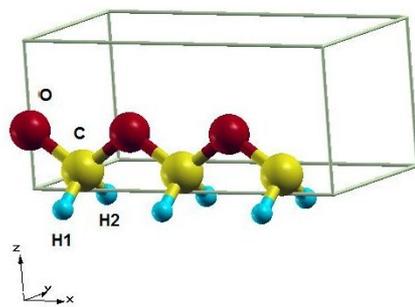Fig. 1(c). Structural pattern of 2NPNH
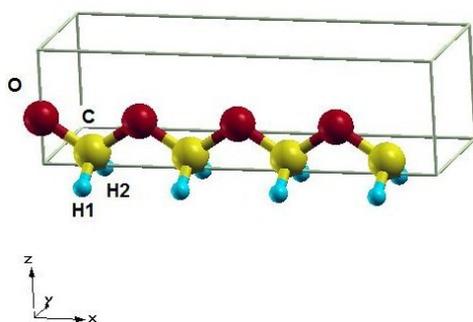

Fig. 1(d). Structural pattern of 3NPNH

Fig. 1(e). Structural pattern of 4NPNH

Looking at the optical phonon modes one can decide that there are two stable conformations for the Polyformaldehyde. First-principles calculations reveal that the helical conformation with four monomers per unit cell is highly acceptable.

"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" [19]. Structure of unit cell in case of helical structure with 4 monomers per unit cell as seen along X, Y and Z axes are given in Figs. 2(a), 2(b) and 2(c) respectively.
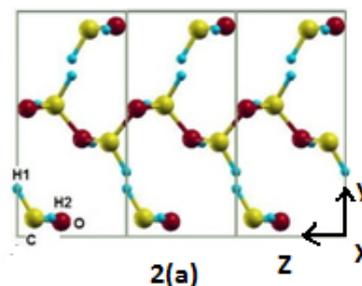
2(a)
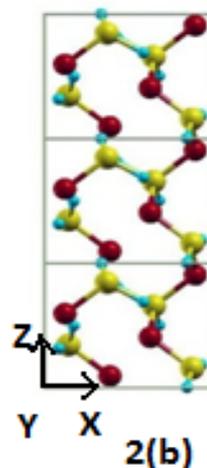
2(b)
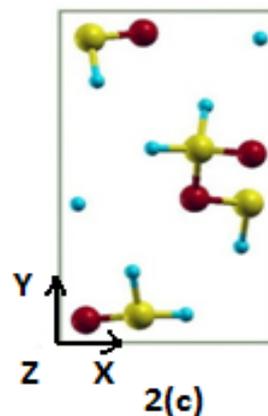
2(c)

Fig.2(a,b,c). Orthorhombic helical Polyformaldehyde viewed along X, Y and Z axes respectively

The Polyformaldehyde under consideration has orthorhombic structure having four monomers per unit cell with lattice parameters a=4.45 Å, b=7.28 Å, c=3.51 Å. Volume of the unit cell is 113.8 $(Å)^3$. The space group of the simulated structure has been found using the ABINIT program and is found to be $P2_12_12_1$. Bond lengths and bond angles in the simulated structure have been tabulated in tables III and IV.

TABLE III
Bond lengths in Polyformaldehyde

Bond	Bond length (Å)
C – O	1.41
C – H	1.11

TABLE IV
Bond angles in Polyformaldehyde

Bond	Bond angle (degree)
O – C – O	112
C – O – C	114
H – C – H	110
H – C – O	106

Conclusion

Structural pattern recognition plays an important role in deciding the structural conformation of molecules. Specially, it is highly essential in case of study of bio-molecules and polymeric systems. FTIR, Raman and Structure simulation techniques have become versatile tools for the structural pattern recognition of molecules.

First-principles calculations clearly indicate that, among various possible conformations of Polyformaldehyde, the one with Orthorhombic unit cell having four monomers per unit cell showing helical structure of molecular arrangement is most stable.

Acknowledgements

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