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Structure Simulation and Study of Electronic and Dielectric Properties of Unfluorinated and Fluorinated 1,4 Lactone

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Abstract

First-principles calculations based on density functional theory have been done on the technologically important organic material 2,3-dideoxy-d-erythro-hex-2-enono-1,4-lactone [$C_6H_8O_4$]. The triclinic structure of the material has been simulated and the structural parameters are found to be a=4.057Å, b=4.263Å, c=8.261Å, α=88.62°, β=80.36°, γ=65.13°. After fluorination the structural parameters are found to be a=4.156Å, b=4.488Å, c=7.652Å, α=83.10°, β=84.51°, γ=84.82°. Electron density of states (EDOS) has been computed in the material using the electronic structure calculation code of quantum-espresso which gives a band gap of 3.17 eV. After fluorination the band gap is found to be 3.14 eV. The value of dielectric constant in the material comes out to be 2.2508, 2.4991 and 2.9935 along x, y and z axes respectively and the average value comes out to be 2.58. After fluorination the dielectric constant of the compound comes out to be 2.3631, 2.3547 and 2.7103 along x, y and z axes respectively and the average value comes out to be 2.48. The computed phonon modes range from 357 cm^{-1} to 3555 cm^{-1}. After fluorination the phonon modes range from 300 cm^{-1} to 3493 cm^{-1}.

Keywords: 1,4-Lactone; First-principles calculation; Electron density of states (EDOS); Band gap; Dielectric constant; Phonon modes

Introduction

Lactones have attracted the scientific community owing to their potential biological applications [1]. Okamura [2] have found L-gulono-1,4-lactone oxidase activity in *Grifola frondosa*. Keates et al. [3] have found that extracts of sclerotia from *Sclerotinia sclerotiorum*, a fungal phytopathogen, contain two electrochemically active constituents, d-glycero-pent-2-enono-1,4-lactone and 5-O-(α-d-galactopyranosyl)-d-glycero-pent-2-enono-1,4-lactone. Robinson et al. [4] have extracted anticancer sesquiterpene lactone from the roots of *Saussurea lappa*.

Huh et al. [5] have characterized D-arabinono-1,4-lactone oxidase obtained from *Candida albicans* ATCC 10231. Nishikimi et al. [6] have studied the cloning and chromosomal mapping of the human nonfunctional gene for L-gulono-gamma-lactone oxidase, the enzyme for L-ascorbic acid biosynthesis which is missing in man. Hervas et al. [7] have studied the communication between L-galactonon-1,4-lactone dehydrogenase and cytochrome c.

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Ostergaard et al. [8] have carried out isolation of a cDNA coding for L-galactono-gamma-lactone dehydrogenase, an enzyme involved in the biosynthesis of ascorbic acid in plants. Imai et al. [9] have extracted L-galactono-gamma-lactone dehydrogenase from mitochondria of sweet potato tuberous roots. Schertl et al. [10] have used L-galactono-1,4-lactone dehydrogenase (GLDH) as a catalyst in the terminal step of the Smirnoff-Wheeler pathway for vitamin C (L-ascorbate) biosynthesis in plants. Fun et al. [11] have studied the structure of 2,3-dideoxy-d-erythro-hex-2-enono-1,4-lactone [1,4-lactone ($C_6H_8O_4$)] using XRD.

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 [12,13]. 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 [14] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of organic materials [15,16]. With this in view, structure of 1,4 Lactone ($C_6H_8O_4$) has been simulated using first-principles calculations based on density functional theory and computation 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 [17]. 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. Authors have used plane wave self-consistent field (PWSCF) [18] implementation of density functional theory (DFT), with a local density approximation (LDA) [19] to exchange correlation energy of electrons and ultra-soft pseudopotentials [20], 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 [21] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme [22] with broadening of 0.03 Ry. The structure was relaxed to minimize energy.

Results and Discussion

In the present study, the triclinic unit cell of 1,4 Lactone was first simulated using “Avogadro” [23]. Later, atomic positions of the molecules 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=4.057Å, b=4.263Å, c=8.261Å, α=88.62°, β=80.36°, γ=65.13°. “scf” calculation was done using the final atomic positions obtained after relaxing the structure using the program 'pw.x' of quantum espresso. Fluorination of 1,4 Lactone was done by replacing one hydrogen atom by fluorine atom. Again the structure was relaxed to minimize the energy and the lattice parameters thus arrived are; a=4.156Å, b=4.488Å, c=7.652Å, α=83.10°, β=84.51°, γ=84.82°.

The completely relaxed structure of the unit cell was visualized using the program “XCrysDen” [24] and the structure of unit cell of 1,4 Lactone as seen along X-axis and Y-axis are shown in FIG. 1-4. The bond lengths and bond angles in the relaxed structure of 1,4 Lactone have been tabulated in TABLES 1 and 2 respectively.

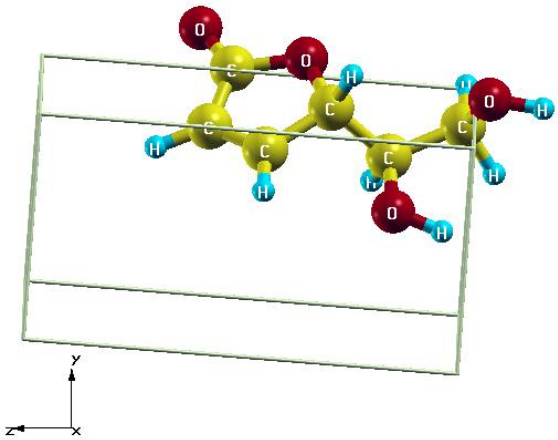

FIG. 1. **Structure of unit cell of 1,4 Lactone as seen along x direction.**

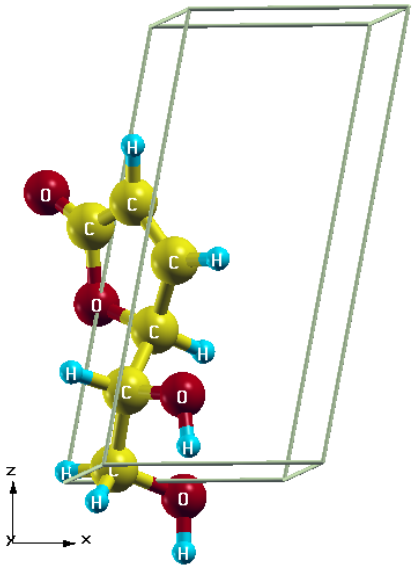

FIG. 2. **Structure of unit cell of 1,4 Lactone as seen along y direction.**

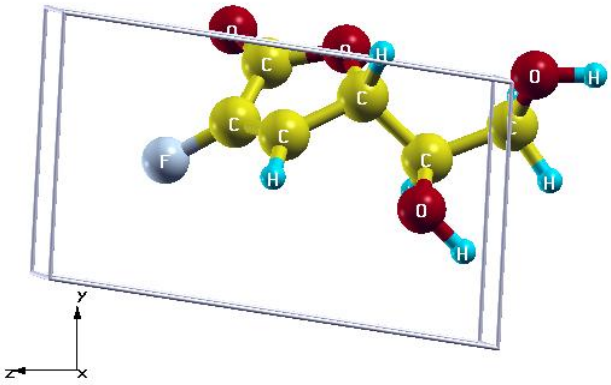

FIG. 3. **Structure of unit cell of fluorinated 1,4 Lactone as seen along x direction.**

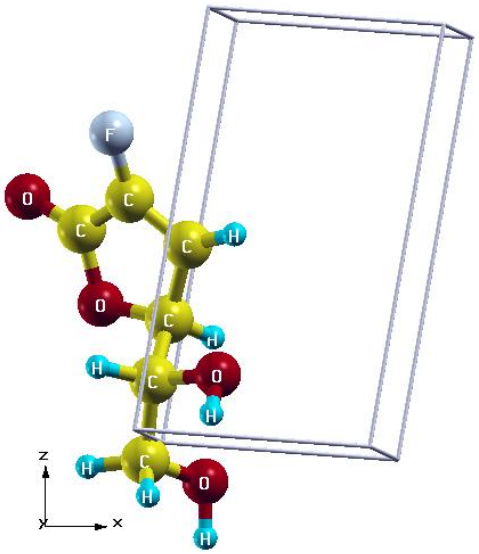

FIG. 4. **Structure of unit cell of fluorinated 1,4 Lactone as seen along y direction.**

TABLE 1. **Bond length in 1,4 Lactone.**

Bond	Bond length (Å)
C–H	1.11
O–H	1.00
C–O	1.24-1.43
C–C	1.37-1.50

TABLE 2. **Bond angle in 1,4 Lactone.**

Bond	Bond angle (deg)
O–C–O	116
H–C–H	107
H–C–C	115, 118
C–O–H	110
C–C–O	111, 112
O–C–H	108, 111
C-C-C	112

EDOS Calculation

Electron density of states (EDOS) has been computed in 1,4 Lactone using electronic structure calculation code of quantum espresso. EDOS in 1,4 Lactone and fluorinated 1,4 Lactone have been shown in FIG. 5 and 6. Band gap in 1,4 Lactone and fluorinated 1,4 Lactone is found to be 3.17 eV and 3.14 eV respectively. This value is close to that exhibited by non-linear optical (NLO) materials [25] and organic semiconducting materials.

Presently, the organic semiconducting materials have very much attracted the scientific community owing to their technological advantages over traditional silicon-based semiconductor devices. Most organic materials are much less expensive to generate than highly crystalline inorganic semiconductors, and also may be used to make devices with inexpensive fabrication methods. Also, most organic materials are soluble in one or more common solvents which allows for the possibility of solution processing which can produce many devices at very low cost [26-28].

Several inorganic NLO materials show a band gap in the range 2 eV to 4 eV. For example, lithium niobate shows a band gap of 4 eV. Barium titanate shows a value of 3.2 eV. BSO crystals show a value of 4.02 eV and KTN nanoparticles show a band gap of 3.2 6eV. The organic NLO material L-Tartaric acid shows an optical band gap of 3.65 eV. Tuning of the band gap plays an important role in the field of photonic crystals.

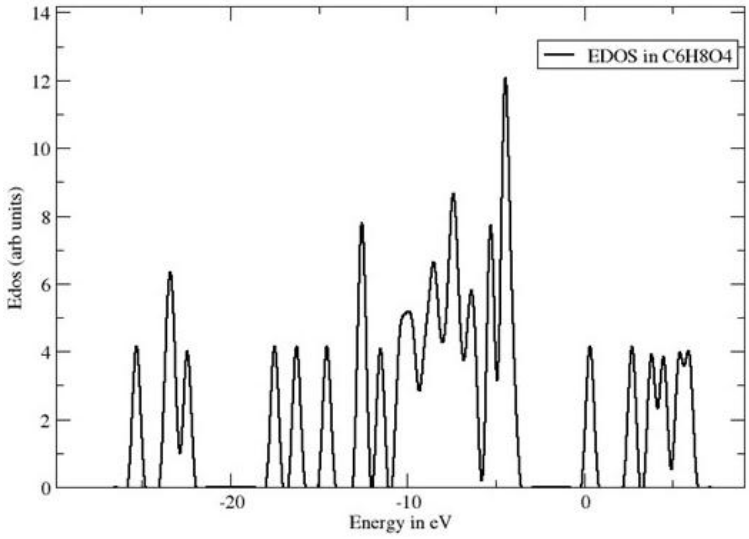

FIG. 5. **Electronic density of states in 1,4 Lactone.**

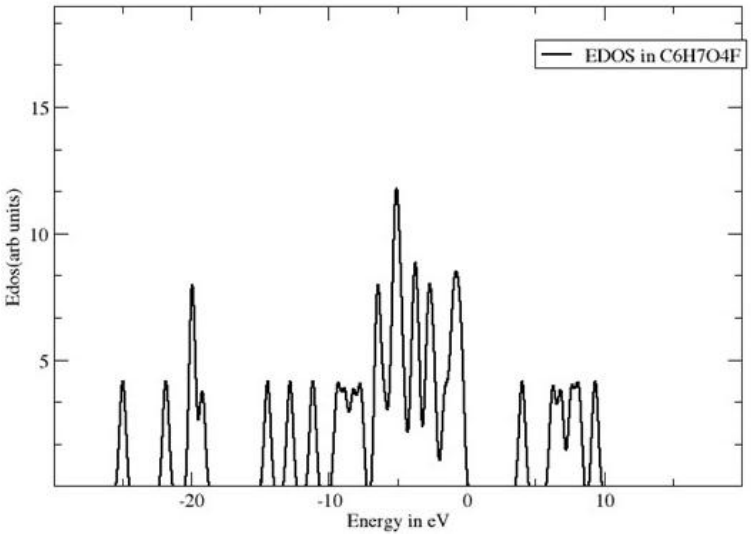

FIG. 6. **Electronic density of states in fluorinated 1,4 Lactone.**

Dielectric constant and phonon modes

The dielectric constant and phonon modes of the material have been computed in unfluorinated and fluorinated state using the ph.x code of quantum espresso. Dielectric constant of the material has been computed. The value of dielectric constant in 1,4 Lactone comes out to be 2.2508, 2.4991 and 2.9935 along x, y and z axes respectively and the average value comes out to be 2.58. After fluorination the dielectric constant of the compound comes out to be 2.3631, 2.3547 and 2.7103 along x, y and z axes respectively the average value comes to be 2.48.

This value is in the range exhibited by low k dielectric materials used in the semiconductor industry. For example; dielectric constant of fluropolyimide is 2.8, benzo-cyclo-butane is 2.7, black diamond is 2.7, polyethylene is 2.4, polypropylene is 2.3, fluoropolymer is 2.24, perylene is 2.2 and in dupont PTFE-based copolymer AF 2400 it is 2.06. They have applications in the fabrication of semiconducting devices [29]. This also shows that the material under study can be used in semiconductor devices.

Phonon modes have been computed using the ph.x program of quantum espresso. The computed phonon modes range from 357 cm^{-1} to 3555 cm^{-1}. After fluorination the phonon modes range from 300 cm^{-1} to 3493 cm^{-1}.

All the phonon modes are positive and hence they clearly prove that the simulated structures are stable. When one hydrogen atom has been replaced by a fluorine atom which is heavier, the frequency range of phonons has come down in the material. Values of various parameters in unfluorinated and fluorinated 1,4 Lactone are tabulated in TABLE 3.

TABLE 3. **Different parameters in unfluorinated and fluorinated 1,4 Lactone.**

Parameter	Unfluorinated 1,4 Lactone	Fluorinated 1,4 Lactone
a (Å)	4.057	4.156
b (Å)	4.263	4.488
c (Å)	8.261	7.652
α (deg)	88.62	83.10
β (deg)	80.36	84.51
γ (deg)	65.13	84.80
Crystal system	Triclinic	Triclinic
Band gap (eV)	3.17	3.14
Average Dielectric constant	2.58	2.48
Phonon modes (cm^{-1})	357-3555	300-3493

Conclusions

The lattice parameters arrived at by the structural optimization using the first-principles calculations are a=4.057Å, b=4.263Å, c=8.261Å, α=88.62°, β=80.36°, γ=65.13°. After flourination lattice parameters are found to be a=4.156Å, b=4.488Å, c=7.652Å, α=83.10°, β=84.51°, γ=84.81°. The lattice parameters of the present study are matching well with the experimentally found values in the material. The material shows a band gap of 3.17 eV. After fluorination the band gap of the material reduces to 3.14 eV. These values of band gap tell that this material is behaving as an organic semiconductor. The material shows an average dielectric constant of 2.58 and after fluorination the average dielectric constant is reduced to 2.48. The computed phonon modes

in the material range from 357 cm^{-1} to 3555 cm^{-1}. After fluorination the phonon modes range from 300 cm^{-1} to 3493 cm^{-1}. Thus it is demanding for further investigations in the material to explore the applications of this material in organic semiconductor electronics and NLO applications. Present study of electronic and dielectric properties of the material is clearly indicating that this material is having the band gap and dielectric constant exhibited by organic semiconducting materials and NLO materials. Also, the present study clearly reveals that the band gap of this material can be tuned by the fluorination.

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