Structure simulation and study of electronic and dielectric properties of urea

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ABSTRACT

First-principles calculations based on Density Functional Theory have been done on the Urea - CH_4N_2O. The Orthorhombic structure of Urea has been simulated and the structural parameters have been found out. Electron Density of States (EDOS) has been computed in the materials using the Electronic structure calculation code of Quantum-Espresso which gives a Band gap of 2.57 eV. This value is close to the value exhibited by NLO materials. Dielectric constant of the materials has been computed. The value of dielectric constant comes out to be 2.14, 2.16 and 2.50 along X, Y and Z axes respectively and the average value comes out to be 2.27.
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INTRODUCTION

Urea or Carbamide is an organic compound with the chemical formula $CO(NH_2)_2$ ie., CH_4N_2O. The molecule has two —NH_2 groups joined by a carbonyl (C=O) functional group. Urea serves an important role in the metabolism of compounds containing nitrogen by animals and is the main nitrogen containing substance in the urine of mammals. It is a colorless, odorless solid, highly soluble in water and practically non-toxic. When dissolved in water, it is neither acidic nor alkaline. The body uses it in many processes, the most notable of them being nitrogen excretion. Urea is widely used in fertilizers as a rich source of nitrogen. Urea is also an important raw material in the chemical industry.

The cycling of urea and also excretion of urea by the kidneys is a vital part of mammalian metabolism. Besides its role as carrier of waste nitrogen, urea also plays an important role in the counter-current exchange system of the nephrons, which allows for reabsorption of water and critical ions from the excreted urine. Urea is reabsorbed in the inner medullary collecting ducts of the nephrons[1]. This results in raising the osmolarity in the medullary interstitium surrounding the thin ascending limb of the loop of Henle, which in turn causes water to be reabsorbed. By action of the urea transporter 2, some of this reabsorbed urea will eventually flow back into the thin ascending limb of the tubule, through the collecting ducts, and into the excreted urine. This mechanism, which is controlled by the antidiuretic hormone, allows the body to create hyperosmotic urine, that has a higher concentration of dissolved substances than the blood plasma. This mechanism is important to prevent the loss of water, to maintain blood pressure, and to maintain a suitable concentration of sodium ions in the blood plasma.

The urea molecule is planar in the crystal structure, but the geometry around the nitrogens is pyra-

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midal in the gasphase minimum energy structure[2]. In solid urea, the oxygen center is engaged in two N-H-O hydrogen bonds. The resulting dense and energetically favourable hydrogen-bond network is probably established at the cost of efficient molecular packing: The structure is quite open, the ribbons forming tunnels with square cross section.

By virtue of its tendency to form a porous framework, urea has the ability to trap many organic compounds. In these compounds which are called as 'clathrates', the organic 'guest' molecules are held in channels formed by interpenetrating helices composed of hydrogen-bonded urea molecules. This behaviour can be used to separate mixtures, e.g. in the production of aviation fuel and lubricating oils, and in the separation of hydrocarbons.

Thus, Urea has wide number of applications in several fields[3-5]. It has been even used even as a biosensor[6]. Any little modification in the structure and composition of a material will bring in sufficient changes in the properties of the material[7, 8]. 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[9] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of organic materials[10, 11]. With this in view, an attempt has been made to look into the structural aspects, Electronic and Dielectric properties of Urea using the First-principles calculations.

Computational details

Several codes are available for the theoretical structure simulation[12]. 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)[13] implementation of density functional theory (DFT), with a Local density approximation (LDA)[14] to exchange correlation energy of electrons and ultrasoft pseudopotentials[15], 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 15 Ry and charge density cutoff of 70 Ry. Integration over Brillouin zone was sampled with a Monkhorst-Pack scheme[16] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme[17] with broadening of 0.03 Ry. The structure was relaxed to minimize energy.

RESULTS AND DISCUSSION

In the present study, the orthorhombic unit cell of Urea was first built using "Avogadro"[18]. The structure was allowed for geometric optimization. Later, atomic positions of the geometrically optimized structure have been used in the plane wave self consistent field calculations.

The structure was relaxed with different values of lattice parameters. Optimized values of lattice parameters thus arrived at through minimization of energy are; a=5.70Å, b=5.91Å and c=4.73Å. "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] and the structure as viewed along X, Y and Z axes are given in Figures 1, 2 and 3. The bond lengths and bond angles in the relaxed structure of Urea have been tabulated in TABLES 1 and 2. Similar values of structural parameters have been found by Henrik Birkedal et. al.,[20] – but with tetragonal unit cell. The carbon in urea is described as sp2 hybridized, the C-N bonds have significant double bond character, and the carbonyl oxygen is basic compared to, say, formaldehyde. The high aqueous solubility of Urea reflects its ability to engage in extensive hydrogen bonding with water.
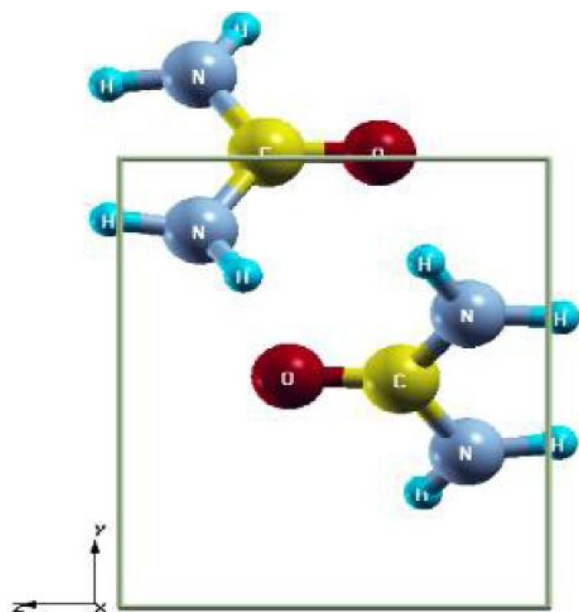
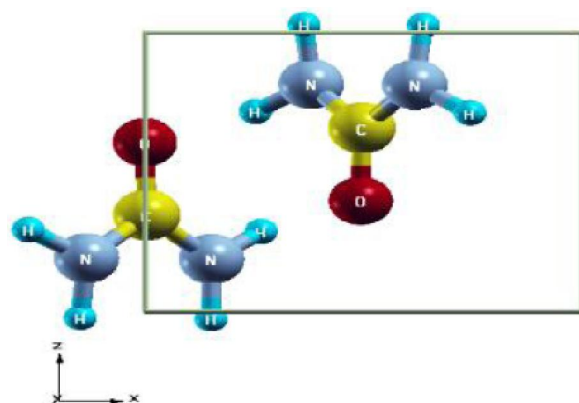**Figure 1 : Structure of urea as viewed along X axis**

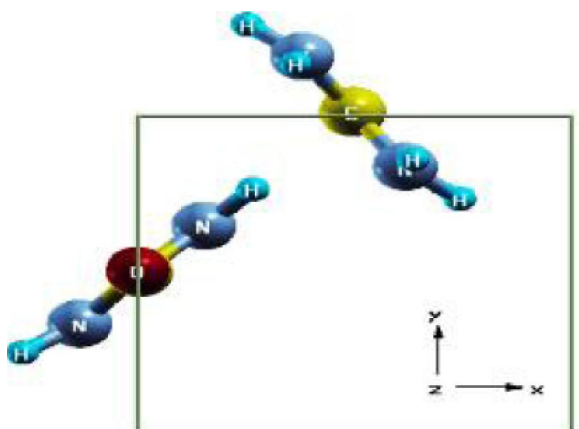**Figure 2 : Structure of urea as viewed along Y axis**

Figure 3 : Structure of urea as viewed along Z axis

EDOS calculation

Electron Density of States (EDOS) have been computed using Electronic structure calculation code

TABLE 1 : Bond lengths in urea

Bond	Bond length (Å)
O-C	1.20
C-N	1.38
N-H	1.01

TABLE 2 : Bond angles in urea

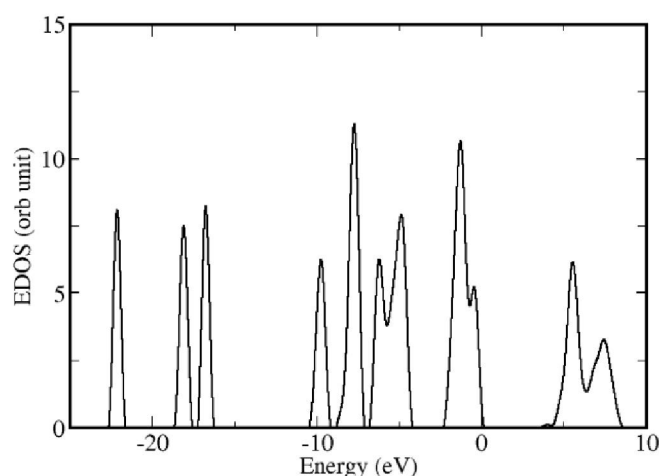|	Bond angle (Deg)
O-C-N	122.2, 121.9
H-N-C	119.1, 120.5, 118.7, 113.8
H-N-H	119.4
H-C-N	115.7

Figure 4 : Electronic density of states in urea

of Quantum espresso and is shown in Figure 4. The band gap comes out to be 2.57 eV. This value is close to the value shown by NLO materials[21] and liquid crystalline materials[22, 23].

Dielectric constant and phonon modes

The value of dielectric constant comes out to be Dielectric constant of the material has been computed and it comes out to be 2.14, 2.16 and 2.50 along X, Y and Z axes respectively and the average value comes out to be 2.27. The computed phonon modes at the gamma point range from 70 cm^{-1} to 3474 cm^{-1} showing that the simulated structure is stable.

CONCLUSIONS

Band gap in case of Urea is found to be 2.57 eV. This value is close to the value shown by NLO materials and liquid crystalline materials. Hence the

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possibility of finding liquid crystalline nature in mixtures containing Urea can be explored. The average value of dielectric constant in Urea comes out to be 2.27. The computed phonon modes at the gamma point range from 70 cm^{-1} to 3474 cm^{-1} showing that the simulated structure is stable.

ACKNOWLEDGMENTS

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