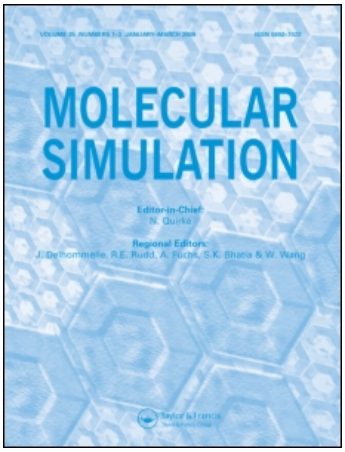

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Theoretical analysis on the structure and properties of thiourea dioxide crystal

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The equilibrium geometry, electronic structure and optical properties of thiourea *S*, *S*-dioxide crystal have been studied using DFT within generalized gradient approximation (GGA) and the local density approximation (LDA), implemented using ultrasoft pseudo-potentials. The optimum bulk geometry is in good agreement with crystallographic data. An analysis of electronic structure, charge and bond order is presented. The energy gap of thiourea dioxide with GGA and LDA calculation is 3.217 or 3.210 eV, respectively, indicating that the compound is an insulator. The calculated absorption spectrum shows a number of absorption peaks, which are believed to be associated with different exciton states, in the fundamental absorption region.

Keywords: Thiourea *S*, *S*-Dioxide (formamidinesulfinic acid, aminoiminomethanesulfinic acid or AIMSA); Density functional theory (DFT); Electronic structure; Optical properties

1. Introduction

There is a considerable amount of interest in thiourea oxides, especially thiourea *S*, *S*-dioxide (formamidinesulfinic acid or aminoiminomethanesulfinic acid, AIMSA) in chemistry and the chemical industry. Since AIMSA was first synthesized, it has been investigated by a number of experimental and theoretical researches [1–14]. AIMSA is widely used as a bleaching agent in the textile industry [6]. In biochemistry, AIMSA is used for the inactivation and modification of synthetase [7–9]. The non-linear kinetics of AIMSA is also studied [10]. So far, there have been several theoretical studies on thiourea dioxide. Yu Wang *et al.* used the EHMO method in an early study of the structure and charge density of thiourea dioxide [11]. Song *et al.* performed HF/3-21G* calculations of molecular electrostatic potential (MEP) of thiourea dioxide monomer and dimers [12]. Makarov and Kudrik studied tautomerization of thiourea dioxide in aqueous solution by the semiempirical AM1 method [13]. Chi-Rung Lee *et al.* published a combined experimental and theoretical study of the electron density of intermolecular interactions in thiourea *S*, *S*-dioxide crystal [14]. However, these were for observed crystal structure and do not shed any light on the structure. Crystalline structures determine crystalline properties. As far as know, there is no report on the optical properties of thiourea dioxide crystal. In this study we use the *ab initio* periodic calculation methods based on DFT to study the equilibrium geometry, electronic structure and optical properties of thiourea dioxide. The atomic positions and the unit cell parameters were allowed to relax to the minimum energy configuration to investigate the crystal structure. Then, we study the electronic structure and optical properties of crystalline thiourea dioxide.

2. Computational methods

The calculations performed in this study were done within the framework of DFT [15] using Vanderbilt-type ultrasoft pseudo-potentials [16] and a plane-wave expansion of the wave functions. The self-consistent ground state of the system was determined using a band-by-band conjugate gradient technique to minimize the total energy of the system with respect to the plane-wave coefficients. The electronic wave functions were obtained by a density-mixing scheme [17] and the structures were relaxed using

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the Broyden, Fletcher, Goldfarb and Shannon (BFGS) method [18]. The generalized GGA with PW91 and LDA with CA-PZ, were employed. The cutoff energy of plane-waves was set to 300.0 eV. Brillouin zone sampling was performed using the Monkhost–Pack scheme with a k point grid of $2 \times 2 \times 5$. The values of the kinetic energy cutoff and the k point grid were determined to ensure the convergence of total energies to within 0.01%.

The thiourea dioxide crystal has an orthorhombic lattice with the space group P_{nma} and contains four molecules per unit cell [1], shown in figure 1. In the crystal, the molecules are linked together by eight hydrogen bonds with four neighbouring molecules. In the geometry relaxation, the total energy of the system was converged less than 1.0×10^{-6} eV, the residual force less than 0.02 eV/Å, the displacement of atoms less than 0.001 Å, and the residual bulk stress less than 0.1 GPa.

3. Results and discussion

3.1 Crystal structure

The full relaxation of the structure was performed to allow the thiourea dioxide molecule configurations, cell shape and volume to change. The partly optimised structural and geometrical parameters of thiourea dioxide bulk using LDA and GGA methods are given in table 1. Note that the GGA slightly increases the lattice constants of bulk thiourea dioxide in comparison with the experiment [1], whereas the LDA slightly reduces the lattice constants. The GGA results give the lattice constants $a = 10.779$ Å, $b = 10.203$ Å, $c = 3.987$ Å, respectively, whereas the LDA values $a = 10.529$ Å, $b = 10.032$ Å, $c = 3.956$ Å, respectively.

From table 1 it can see that the LDA and GGA calculated bond lengths for thiourea dioxide are very close for experimental values. Usually, the strength of hydrogen bond dominates intensity of intermolecular interactions. The O . . . H lengths vary from 1.747 to 2.061 Å, indicating that there exist strong H-bonds in the thiourea dioxide crystal. However, our calculated hydrogen bonds of LDA are shorter than that of GGA and experiment, indicating LDA overestimates hydrogen bond interaction. Both GGA and LDA results show that each thiourea dioxide molecule is involved in eight hydrogen bonds between four neighbouring molecules, shown in figure 2.

Table 1. Cell and geometrical parameters (Å) for thiourea dioxide crystal.

Parameters	*GGA*	*LDA*	*Exp* [1]
a	10.779	10.529	10.644
b	10.203	10.032	10.106
c	3.987	3.956	3.935
N—H1	1.038	1.056	1.027
N—H2	1.031	1.05	1.024
N—C	1.308	1.309	1.297
C—S	1.865	1.846	1.862
S—O	1.504	1.508	1.489
O . . . H1	1.819	1.747	1.822
O . . . H2	1.894	1.778	2.061

3.2 Electronic structure

The energy band structure of crystalline thiourea dioxide with GGA and LDA is shown in figure 3. The origin of the energy is taken to be the Fermi level. Both the upper valence bands (the highest occupied crystal orbitals, HOCO) and lower conduction bands (the lowest unoccupied crystal orbitals, LUCO) are generally quite flat. As shown in figure 3(a), the valence band maximum is at G point, and the conduction band minimum is at Z point. The indirect band gap between these two points is calculated to be 2.920 eV, the smallest direct gap is found to be 3.217 eV. The result of LDA is very similar with that of GGA. The energy gap with LDA is 3.210 eV. These

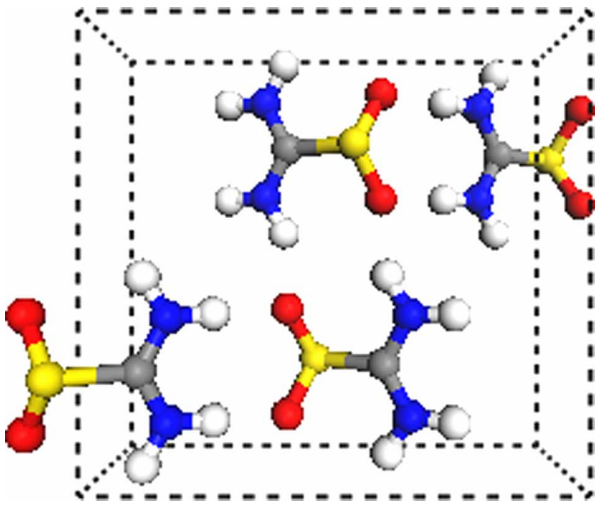

Figure 1. The packing of thiourea dioxide in unit cell; carbon, nitrogen, oxygen, sulfur and hydrogen atoms are represented by the colors of gray, blue, red, yellow and white, respectively.

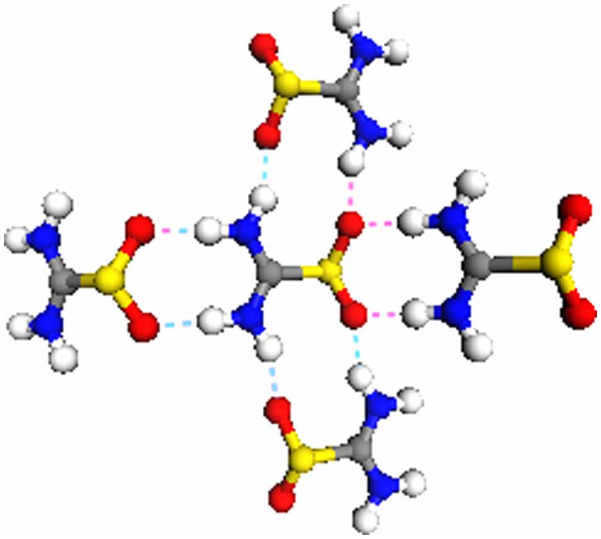

Figure 2. Thiourea dioxide are depicted in order to show the hydrogen bonds with four neighbouring molecules.

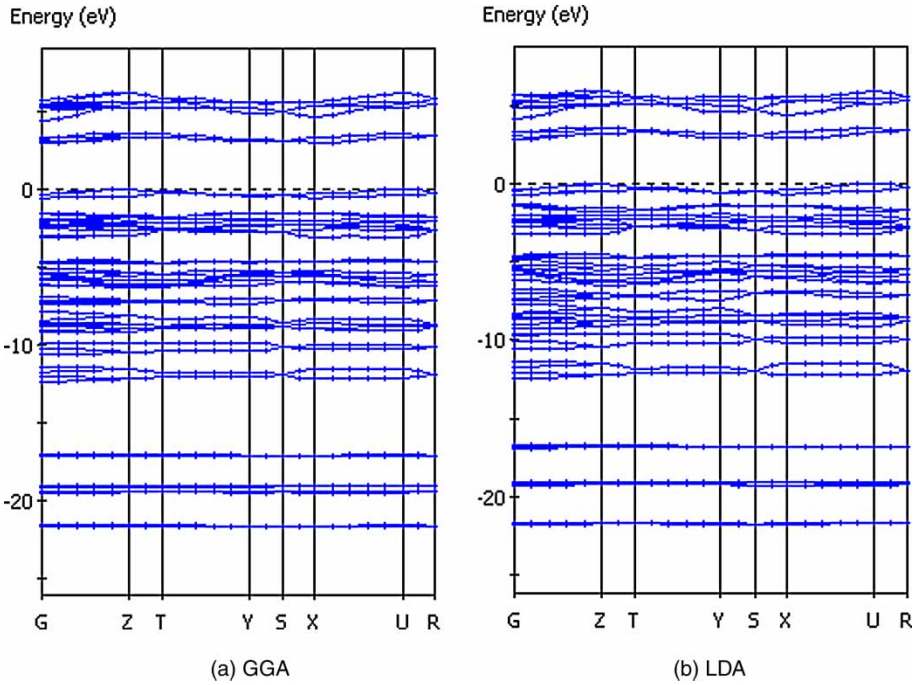

Figure 3. Energy band structure of thiourea dioxide using (a) GGA and (b) LDA.

values indicate that the compound is an insulator, which is in agreement with the experimental result.

The electronic structure can be further analysed by examining the Mulliken charge and bond order in thiourea dioxide. Table 2 shows the charge and bond order values for thiourea dioxide. Note that the results of Mulliken charge and bond order of thiourea dioxide using GGA are in agreement with results using LDA. From table 2 one can see that the carbon, hydrogen and sulfur atoms are positively charged, while oxygen and nitrogen atoms are negatively charged. The thiourea part of thiourea dioxide is positively charged, while SO_2 fragment is negatively charged.

3.3 Optical properties

In this section, we turn to investigate the optical properties of thiourea dioxide. The interaction of a photon with the electrons in the system can result in transitions between occupied and unoccupied states. The spectra resulting from these excitations can be described as a joint density of states between the valence and conduction bands. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function can be obtained from the momentum matrix elements between the occupied and unoccupied wave functions within the selection rules, and the real part $\varepsilon_1(\omega)$ of dielectric function can be calculated from imaginary part $\varepsilon_2(\omega)$ by Kramer–Kronig relationship. Absorption coefficient $\alpha(\omega)$ can be evaluated from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ [19].

$$\alpha(\omega) = \sqrt{2}\omega\left(\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)\right)^{1/2} \quad (1)$$

The absorption coefficient α (ω) of thiourea dioxide with GGA and LDA are plotted in figure 4. Both results of GGA and LDA are very similar. The first absorption peak in α (ω) spectra is found near 3.6 eV. The absorption coefficient of the band at 6.0 eV is estimated by our calculations to be $0.5 \times 10^7\,\mathrm{m}^{-1}$. We also note that thiourea dioxide has a very strong adsorption at 8.1 and

Table 2. Mulliken charges (e) and bond orders of thiourea dioxide crystal.

Charge	*GGA*	*LDA*	*Bond order*	*GGA*	*LDA*
O	−0.98	−0.96	S—O	0.36	0.36
S	1.48	1.46	C—S	0.36	0.39
C	0.22	0.21	N—C	0.96	0.98
N	−0.80	−0.76	N—H1	0.64	0.64
H1	0.48	0.45	N—H2	0.62	0.61
H2	0.46	0.43			

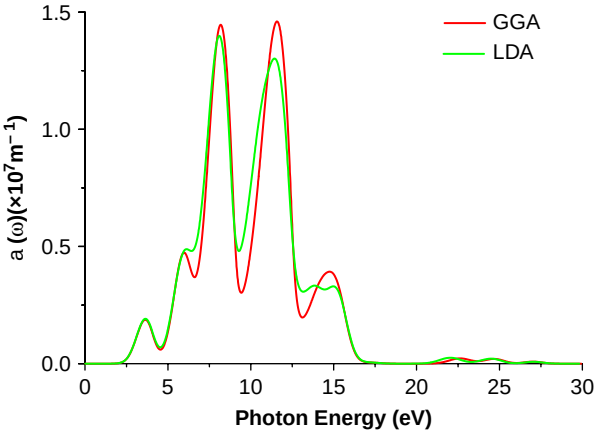

Figure 4. Absorption coefficient α for the thiourea dioxide using GGA and LDA.

11.5 eV. The magnitude of the absorption coefficients of these peaks allows an optical transition due to excitons. Since the absorption coefficient in the fundamental region is very high ($10^7\,m^{-1}$), thiourea dioxide is unstable and decomposes under the action of light and heat. In conclusion, it is found that the absorption spectrum of thiourea dioxide displays a number of absorption peaks, which are believed to be associated with different exciton states, in the fundamental absorption region.

4. Conclusions

From the DFT calculations to investigate the structural, electronic and optical of thiourea dioxide reported in the paper, the following conclusions can be drawn:

(1) The crystal structures of thiourea dioxide compare well with experimental data. There exist lots of strong H-bonds in the thiourea dioxide crystal. Moreover, it is found LAD overestimates hydrogen bond interaction.
(2) An analysis of electronic structure, charge and bond order is presented. It exhibits a energy gap of 3.217 or 3.210 eV between valence and conduction bands, indicating that the compound is an insulator.
(3) The absorption spectrum of thiourea dioxide shows a number of absorption peaks, which are believed to be associated with different exciton states, in the fundamental absorption region.

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