



# Reactivities of some thiol collectors and their interactions with Ag (+1) ion by molecular modeling

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## Abstract

The most commonly used collectors for sulfide minerals in the mining industry are the thiol collectors for the recovery of these minerals from their associated gangues by froth flotation. For this reason, a great deal of attention has been paid to understand the attachment mechanism of thiol collectors to metal sulfide surfaces. The density functional theory (DFT) calculations at the B3LYP/3-21G\* and B3LYP/6-31++G\*\* levels were employed to propose the flotation responses of these thiol collectors, namely, diethyl dithiocarbamate, ethyl dithiocarbamate, ethyl dithiocarbonate, ethyl trithiocarbonate and ethyl dithiophosphate ions, and to study the interaction energies of these collectors with Ag (+1) ion in connection to acanthite (Ag<sub>2</sub>S) mineral. The calculated interaction energies,  $\Delta E$ , were interpreted in terms of the highest occupied molecular orbital (HOMO) energies of the isolated collector ions. The results show that the HOMOs are strongly localized to the sulfur atoms and the HOMO energies can be used as a reactivity descriptor for the flotation ability of the thiol collectors. Using the HOMO and  $\Delta E$  energies, the reactivity order of the collectors is found to be  $(C_2H_5)_2NCS_2^- > C_2H_5NHCS_2^- > C_2H_5OCS_2^- > C_2H_5SCS_2^- > (C_2H_5O)(OH)PS_2^-$ . The theoretically obtained results are in good agreement with the experimental data reported.

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## 1. Introduction

Flotation reagents used in the flotation of minerals are classified into three types, which are collectors, frothers and regulators. Collectors are the reagents that render the valuable mineral hydrophobic for better floatability. They are usually surface-active compounds and many of them (short-chain thiol

compounds) are not surface active at the water–air interface. They contain a polar group in hydrophilic character and non-polar group in hydrophobic character that attach to the air bubbles in the flotation cells. Therefore, collectors are the most important element of the flotation process that are used for the separation of minerals from their ores, and they also can be divided into several classes depending on anionic, cationic or other molecular characteristics. Thiol collectors such as alkyl dithiocarbonate (xanthate), dithiophosphate and dithiocarbamate ions are widely used in the flotation of the valuable sulfide minerals

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### Nomenclature

$E_{\text{complex}}$	electronic energy of the collector–Ag <sup>+</sup> complex (hartree)
$E_{\text{Ag}^+}$	electronic energy of Ag <sup>+</sup> ion (hartree)
$E_{\text{collector}}$	electronic energy of collector (hartree)
$\Delta E$	interaction energies (hartree and kcal mol <sup>-1</sup> )
HOMO	the highest occupied molecular orbital energy (eV)
LUMO	the lowest occupied molecular energy (eV)
$r$	bond length (Å°)
$\angle$	bond angle (°)
$\tau$	dihedral angle (°)

[1]. Although several mechanisms have been proposed for the flotation of sulfide minerals, the reactions between the thiol collectors and the sulfides of transition and heavy metals are not fully understood [2,3]. Therefore, a number of spectroscopic methods have been employed to understand the interaction mechanisms [4–9].

Computational methods are valuable tools for understanding the chemical systems and prediction of their physicochemical properties. The use of the density functional theory (DFT) methods has grown considerably in the last years in many fields. It is well known that DFT methods require less computational effort than the ab initio calculations, and it has become an alternative to the second-order Møller–Plesset perturbation theory (MP2) which is an approach to the computation of electron correlation energy.

In this paper, we present the DFT results from the investigation of the structural properties, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies of some thiol collectors and their interactions with Ag (+1) ion. We intend to get valuable and predictive information about the most important part of the flotation process of sulfide minerals with an example of acanthite (Ag<sub>2</sub>S) by this approach. Although, as far as, there is no computational study on the interaction of thiol collectors with Ag (+1) ion, several studies have been performed on the related systems [10–12].

## 2. Computational method

In the search of the lowest energy conformation, the potential energy surfaces of the thiols under consideration were scanned using the B3LYP/3-21G\* method [13] and the obtained geometries have been further optimized. Since there is a restriction using the larger basis sets rather than 3-21G\* for silver element, the interaction energies of the collectors with Ag (+1) ion and the properties of the complexes were evaluated with the 3-21G\* basis set. On the other hand, the use of 6-31++G\*\* basis set containing the polarization and diffuse functions for hydrogen and heavy atoms is required for anions. Therefore, for only collector ions, the HOMO–LUMO energies and geometrical parameters were calculated using both the 3-21G\* and 6-31++G\*\* basis sets for comparison.

Electrostatic charge properties of the collector compounds were also theoretically determined. Atomic partial charges calculated according to the scheme of Mulliken [14] and molecular electrostatic potential (MEP)-derived charges were obtained using the CHelpG procedure [15]. The Gaussian 98W [16] was used for all calculations, while GaussView 2.1 [17] program package was used to draw the HOMOs. The interaction energies,  $\Delta E$ , were calculated using the equation given below, and they were not corrected for the basis set superposition error (BSSE).

$$\Delta E = E_{\text{complex}} - [E_{\text{Ag}^+} + E_{\text{collector}}]$$

where  $E_{\text{complex}}$  is electronic energy of the collector–Ag<sup>+</sup> complex (hartree),  $E_{\text{Ag}^+}$  is electronic energy of Ag (+1) ion (hartree) and  $E_{\text{collector}}$  is electronic energy of collector (hartree).

## 3. Results and discussion

Diethyl dithiocarbamate [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCS<sub>2</sub><sup>-</sup>], ethyl dithiocarbamate [C<sub>2</sub>H<sub>5</sub>NHCS<sub>2</sub><sup>-</sup>], ethyl dithiocarbamate (or xanthate) [C<sub>2</sub>H<sub>5</sub>OCS<sub>2</sub><sup>-</sup>], ethyl trithiocarbamate [C<sub>2</sub>H<sub>5</sub>SCS<sub>2</sub><sup>-</sup>] and ethyl dithiophosphate [(C<sub>2</sub>H<sub>5</sub>O)(OH)PS<sub>2</sub><sup>-</sup>] ions were chosen as collectors because of their widely use in the flotation of sulfide minerals. It is believed that the sodium or potassium salts of the collector ions are ionized in aqueous solution and adsorbed on the mineral surfaces as



Y =  $-\text{N}(\text{C}_2\text{H}_5)_2$ ;  $-\text{NHC}_2\text{H}_5$ ;  $-\text{OC}_2\text{H}_5$ ;  $-\text{SC}_2\text{H}_5$

Fig. 1. Schematic representation of the metal–sulfur bonding in the thiol collectors.

$\text{Y-CS}_2^-$  ions. The describing and modeling of the flotation process for any mineral are so complicate. Additionally, the modeling of transition metal complexes is a difficult task. Therefore, in this study, the system has been considered as the collector ions that interact with the Ag (+1) ion in connection to acanthite mineral as shown in Fig. 1.

This kind of interaction cannot be totally true, but qualitative information can be obtained about the interaction energies of the collectors and acanthite. Some results about these type collector–metal interactions can be summarized as following: Winter [18] pointed out that xanthate can be attached to a metal atom in the sulfide surface and can form bonds with sulfur. Metal-xanthates show strong characteristic absorption bands around 1200, 1000 and  $400\text{ cm}^{-1}$ , which are usually identified, as the C–O, C–S and M–S regions [19]. Woods and Hope [7] have applied Raman and  $^{13}\text{C}$  NMR spectroscopies to characterize the ethyl xanthates of silver and other some metals, and proposed that there was a strong metal–sulfur bond strength in the investigating compounds. Persson [20] reported that acanthite mineral forms solid  $\text{AgX}$  compounds (X: alkyl xanthate and alkyl dithiophosphate ions) without oxidizing the collectors to alkyl dixanthogens and bis (alkyl dithiophosphoryl) disulfides. Also, these types of collectors form four-membered rings with the metal ions, with both sulfurs bonded to the metal [21].

Thiol collectors usually act as bidentate ligand and have a negative charge on sulfur atom. Three resonance structures can be written as given in Fig. 2. The importance of the resonance form (III) has been discussed and revealed that (III) form makes an appreciable contribution to the electronic structures of dithiocarbamates, but little contribution to the analogues xanthate systems [21]. The chemical properties of the dithiophosphate collectors are similar to those of the xanthates and reacts in similar way [22].

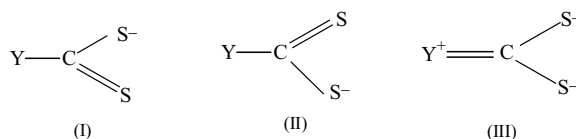


Fig. 2. Schematic representation of the resonance structures for the thiol collectors.

Selected optimized geometrical parameters for the collectors and their complexes with Ag (+1) ion are listed in Table 1. The optimized complex structures are presented in Fig. 3. As already mentioned, the thiol collectors as sulfur donor chelates and their metal complexes have been subject of numerous studies. A comparison of the collector ion structures with each other reveals interesting facts. Unlike expected, the collector ions (except  $(\text{C}_2\text{H}_5)_2\text{NCS}_2^-$ ) contain two significantly different C–S bonds. This observation was also reported by Coucoucovanis [23,24]. From Table 1, it is worth to mention that there is a very good correspondence between the 3-21G\* and 6-31++G\*\* calculated geometrical parameters of the collector ions. For example, the 3-21G\* optimized value for the both of C–S bond in diethyl dithiocarbamate is  $1.766\text{ \AA}$ , and the S–C–S angle is  $123.48^\circ$ . The respective 6-31++G\*\* calculated values are  $1.728$  and  $122.82\text{ \AA}$ , respectively. The author of the review study [23,24] reported that the experimentally measured values of  $r(\text{C-S}) = 1.72\text{ \AA}$  and  $r(\text{C-N}) = 1.34\text{ \AA}$  for the dithiocarbamate ions. The standard single and double  $r(\text{C-N})$  bond lengths are  $1.47$  and  $1.38\text{ \AA}$ , respectively. The results show the presence of the double bond character in the C–N bond. The similar result was also obtained for ethyl dithiocarbamate. In the mean time, as seen in Table 1, the C–N bond of  $\text{C}_2\text{H}_5\text{NHCS}_2^-$  is shorter than that of  $(\text{C}_2\text{H}_5)_2\text{NCS}_2^-$ . This can be explained that the N atom in  $\text{C}_2\text{H}_5\text{NHCS}_2^-$  has more negative charge that of  $(\text{C}_2\text{H}_5)_2\text{NCS}_2^-$  (see Table 2). We can expect the similar delocalization for the C–O bond in  $\text{C}_2\text{H}_5\text{OCS}_2^-$  ion. However, both the experimental data reported in the literature [21] and our results showed that C–O bond has less double bond character. As already known, the standard single and double  $r(\text{C-O})$  bond lengths are  $1.43$  and  $1.21\text{ \AA}$ , respectively. Experimentally obtained bond lengths and bond angle for ethyl xanthate ion were given as  $r(\text{C-S}) = 1.67$  and  $1.70\text{ \AA}$ ;  $r(\text{C-O}) = 1.35\text{ \AA}$  and  $\angle\text{S-C-S} = 124^\circ$  by

Table 1  
Selected optimized geometrical parameters<sup>a</sup> for the collector ions and the collector–Ag complexes at the B3LYP/3-21G\* level

Species	$r(\text{C-S})$ or $r(\text{P-S})$	$r(\text{C-S})$ or $r(\text{P-S})$	$r(\text{C-X}^{\text{b}})$ or $r(\text{P-O})$	$r(\text{S-Ag})$	$r(\text{S-Ag})$	$\angle\text{S-C-S}$ or $\angle\text{S-P-S}$	$\angle\text{S-Ag-S}$	$\tau(\text{C-S-Ag-S})$ or $\tau(\text{P-S-Ag-S})$
$(\text{C}_2\text{H}_5)_2\text{NCS}_2^-$	1.726 (1.728 <sup>c</sup> )	1.726 (1.728)	1.400 (1.389)	–	–	123.48 (122.82)	–	–
$(\text{C}_2\text{H}_5)_2\text{NCS}_2^- \text{Ag}^+$	1.751	1.751	1.353	2.583	2.582	121.96	72.72	–0.01
$\text{C}_2\text{H}_5\text{NHCS}_2^-$	1.725 (1.727)	1.719 (1.717)	1.387 (1.379)	–	–	126.69 (126.46)	–	–
$\text{C}_2\text{H}_5\text{NHCS}_2^- \text{Ag}^+$	1.746	1.739	1.349	2.582	2.599	124.14	72.90	0.81
$\text{C}_2\text{H}_5\text{OCS}_2^-$	1.692 (1.699)	1.701 (1.707)	1.424 (1.383)	–	–	128.82 (127.82)	–	–
$\text{C}_2\text{H}_5\text{OCS}_2^- \text{Ag}^+$	1.721	1.721	1.361	2.583	2.619	126.12	72.29	–0.02
$\text{C}_2\text{H}_5\text{SCS}_2^-$	1.695 (1.697)	1.690 (1.695)	1.832 (1.822)	–	–	129.39 (128.48)	–	–
$\text{C}_2\text{H}_5\text{SCS}_2^- \text{Ag}^+$	1.720	1.712	1.756	2.600	2.630	125.57	71.39	–0.01
$(\text{C}_2\text{H}_5\text{O})(\text{OH})\text{PS}_2^-$	1.978 (1.999)	1.970 (1.992)	P–OH = 1.660; P–OC <sub>2</sub> H <sub>5</sub> = 1.650	–	–	123.36 (123.71)	–	–
$(\text{C}_2\text{H}_5\text{O})(\text{OH})\text{PS}_2^- \text{Ag}^+$	2.011	2.009	P–OH = 1.630; P–OC <sub>2</sub> H <sub>5</sub> = 1.610	2.606	2.611	119.62	83.53	7.54

<sup>a</sup> Bond distances in Å, bond angles in degrees.

<sup>b</sup> X: heteroatom bonded to the  $-\text{CS}_2^-$  (N, O or S).

<sup>c</sup> B3LYP/6-31++G\*\* calculated values given in the parenthesis.

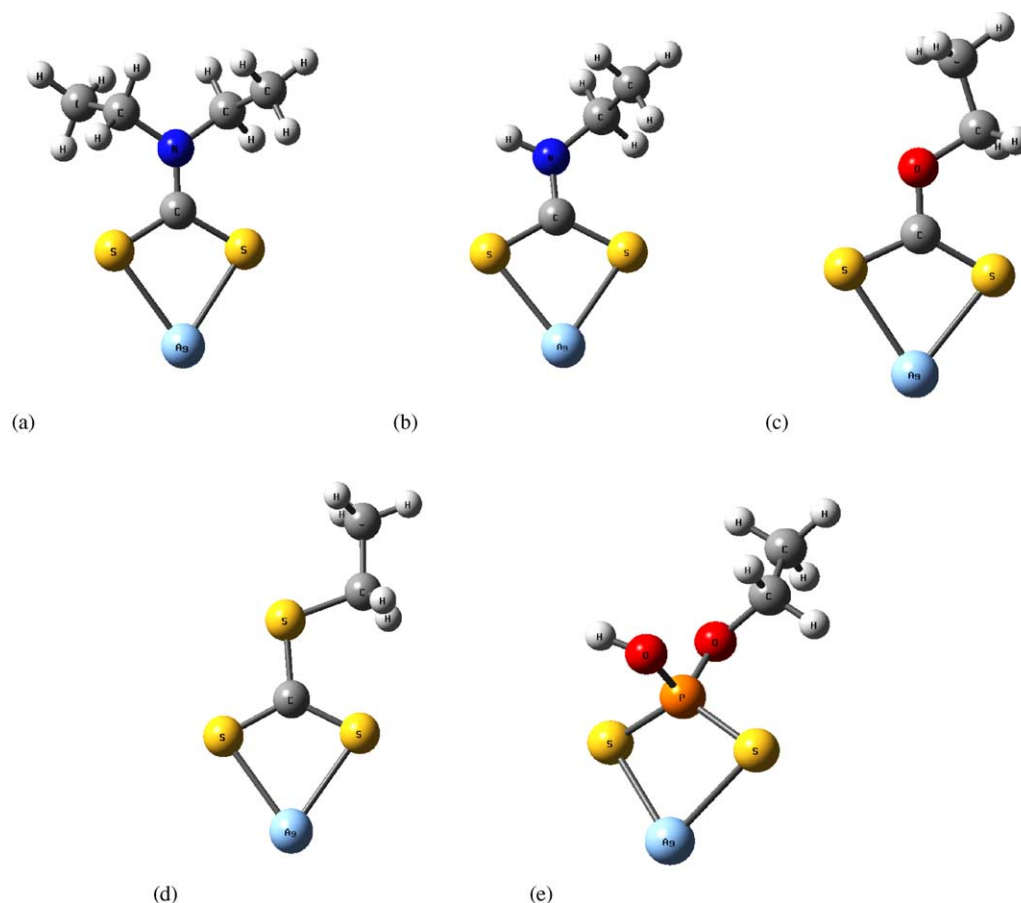


Fig. 3. Optimized geometries of the collector–Ag complexes at the B3LYP/3-21G\* level. (a) Diethyl dithiocarbamate; (b) ethyl dithiocarbamate; (c) ethyl dithiocarbonate (xanthate); (d) ethyl trithiocarbonate; (e) ethyl dithiophosphate.

Winter [19]. As easily seen in Table 1, our calculated values are in good agreement with the experimental values. In the case of  $C_2H_5SCS_2^-$  ion,  $r(C-S) = 1.832 \text{ \AA}$  at the 3-21G\* level and  $1.822 \text{ \AA}$  at the 6-31++G\*\* level which are completely the same with the standard single C–S bond distance ( $1.82 \text{ \AA}$ ). As a result of the  $\pi$ -bonding between 3p orbitals of the sulfur atom and 2p orbitals of the carbon atom is less effective than the one between 2p orbitals of the oxygen atom and 2p orbitals of the carbon atom, the C–O bond of ethyl xanthate ion has more double bond character than the C–S bond of ethyl trithiocarbonate ion. For  $(C_2H_5O)(OH)PS_2^-$  ion, experimentally measured P–S bond distance is  $1.96 \text{ \AA}$ , which is closer to the double bond value of  $1.94 \text{ \AA}$  [21]. The

calculated values for both of P–S bonds  $1.978$  and  $1.970 \text{ \AA}$  at the 3-21G\* level.

The optimized geometries of the complexes studied are seen in Fig. 3. The calculations show that all the C–X and P–O bond distances in the complex structures are shorter than that of in the collector ions as a result of the double bonding between the heteroatom (N, O or S) and carbon. On the other hand, as the C–X (or P–O) bond distances increase, the S–Ag bond distances increase in the complexes. Experimentally measured S–Ag bond length is  $2.49 \text{ \AA}$  for dithiocarbamate–Ag complex and  $2.679 \text{ \AA}$  (the other one is  $2.868 \text{ \AA}$ ) for dithiophosphate–Ag complex [20]. The calculated S–Ag bond distances of the corresponding complexes agree well with the experimental values. The strength

Table 2  
Selected Mulliken<sup>a</sup> and CHelpG<sup>b</sup> charges of the collector ions

Atom	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCS <sub>2</sub> <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> NHCS <sub>2</sub> <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> OCS <sub>2</sub> <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> SCS <sub>2</sub> <sup>-</sup>	(C <sub>2</sub> H <sub>5</sub> O)(OH)PS <sub>2</sub> <sup>-</sup>
B3LYP/3-21G*					
Mulliken					
S	-0.3921	-0.4248	-0.3447	-0.2980	-0.6419
S	-0.3922	-0.3967	-0.3723	-0.2994	-0.6120
X <sup>c</sup>	-0.5681	-0.6327	-0.4838	0.1859	-
CHelpG					
S	-0.6005	-0.6692	-0.6153	-0.5511	-0.6554
S	-0.6002	-0.6019	-0.6172	-0.5586	-0.6174
X <sup>c</sup>	-0.0552	-0.4006	-0.4707	-0.3590	-
B3LYP/6-31++G**					
Mulliken					
S	-0.4752	-0.4264	-0.4040	-0.6093	-0.4965
S	-0.4752	-0.3103	-0.3786	-0.4280	-0.4567
X <sup>c</sup>	0.0575	-0.0793	-0.1634	-0.2220	-
CHelpG					
S	-0.6636	-0.7326	-0.6946	-0.6205	-0.6335
S	-0.6636	-0.6756	-0.6741	-0.6178	-0.5946
X <sup>c</sup>	-0.1929	-0.5117	-0.5601	-0.4327	-

<sup>a</sup> Units in electron.

<sup>b</sup> Units in electron.

<sup>c</sup> X: heteroatom bonded to the -CS<sub>2</sub><sup>-</sup> (N, O or S).

of the metal–sulfur bond is important, since a stronger S–Ag bond corresponds to the stable complexes. The theoretically predicted interaction energies,  $\Delta E$ , are listed in order of descending absolute value in Table 3. The values of the  $\Delta E$  can be explained in terms of the different S–Ag bond distances. As anticipated, the interactions of the Ag (+1) ion with (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCS<sub>2</sub><sup>-</sup>, C<sub>2</sub>H<sub>5</sub>NHCS<sub>2</sub><sup>-</sup> and C<sub>2</sub>H<sub>5</sub>OCS<sub>2</sub><sup>-</sup> collectors are favored over C<sub>2</sub>H<sub>5</sub>SCS<sub>2</sub><sup>-</sup> and (C<sub>2</sub>H<sub>5</sub>O)(OH)PS<sub>2</sub><sup>-</sup> collectors due to the formation of the stronger S–Ag bonds. For this reason, in this study, these ions were found to be

powerful collectors that were already proposed experimentally [1,4,5]. The thiol collectors form four-membered rings with metals using both sulfur atoms. As it may be expected, four-membered rings, such as cyclobutane, are highly strained structures and they change their bond and dihedral angles to decrease the ring strain. In Table 1, it is seen that only minor differences are found in the geometrical parameters of the complexes, except (C<sub>2</sub>H<sub>5</sub>O)(OH)PS<sub>2</sub><sup>-</sup>Ag<sup>+</sup> complex. The  $\angle$ S–C–S (including  $\angle$ S–P–S as well) angles are in the range of 119.62–126.12° and decrease as result of the

Table 3  
HOMO–LUMO (eV) energies of the collector ions, and their interaction energies ( $\Delta E$ ; kcal mol<sup>-1</sup>) with Ag (+1) ion

The collector ions	B3LYP/3-21G*			B3LYP/6-31++G**	
	HOMO	LUMO	$\Delta E$	HOMO	LUMO
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCS <sub>2</sub> <sup>-</sup>	0.0019	0.1650	-175	-0.0217	0.0806
C <sub>2</sub> H <sub>5</sub> NHCS <sub>2</sub> <sup>-</sup>	0.0003	0.1700	-174	-0.0266	0.0788
C <sub>2</sub> H <sub>5</sub> OCS <sub>2</sub> <sup>-</sup>	-0.0064	0.1536	-167	-0.0297	0.0840
C <sub>2</sub> H <sub>5</sub> SCS <sub>2</sub> <sup>-</sup>	-0.022	0.1290	-164	-0.0428	0.0799
(C <sub>2</sub> H <sub>5</sub> O)(OH)PS <sub>2</sub> <sup>-</sup>	-0.0366	0.2090	-163	-0.0616	0.0829

complexation process. The  $\tau(\text{C-S-Ag-S})$  angles are also in the range of  $-0.02$ – $0.81$  showing the four-membered ring lay approximately in the plane. In the case of  $(\text{C}_2\text{H}_5\text{O})(\text{OH})\text{PS}_2^- \text{Ag}^+$  complex,  $\tau(\text{P-S-Ag-S})$  angle indicates that its Ag atom is bent at an angle of  $7.54^\circ$  from the plane of the other three atoms. That is, the ring is not stable as much as the others.

Atomic charges are known as an important factor in intermolecular interactions. In general, the atomic charges at the binding site of the collectors are expected to be described the reactivity of molecules toward formation of the complexes with metal ions.

However, in this study, neither Mulliken nor CHelpG atomic charges (see Table 2) can be successfully used for the describing of the collector reactivities. The theoretical results show that there is no clear dependence between the  $\Delta E$  and the sulfur atomic charges. On the other hand, molecular orbital energies, as listed in Table 3, can provide important clues about the chemical reactivity. The HOMO and LUMO orbitals of a molecule are known as frontier orbitals, and most chemical reactions involve electron movement between them. Therefore, the understanding of these two orbitals is very important for the reacting systems.

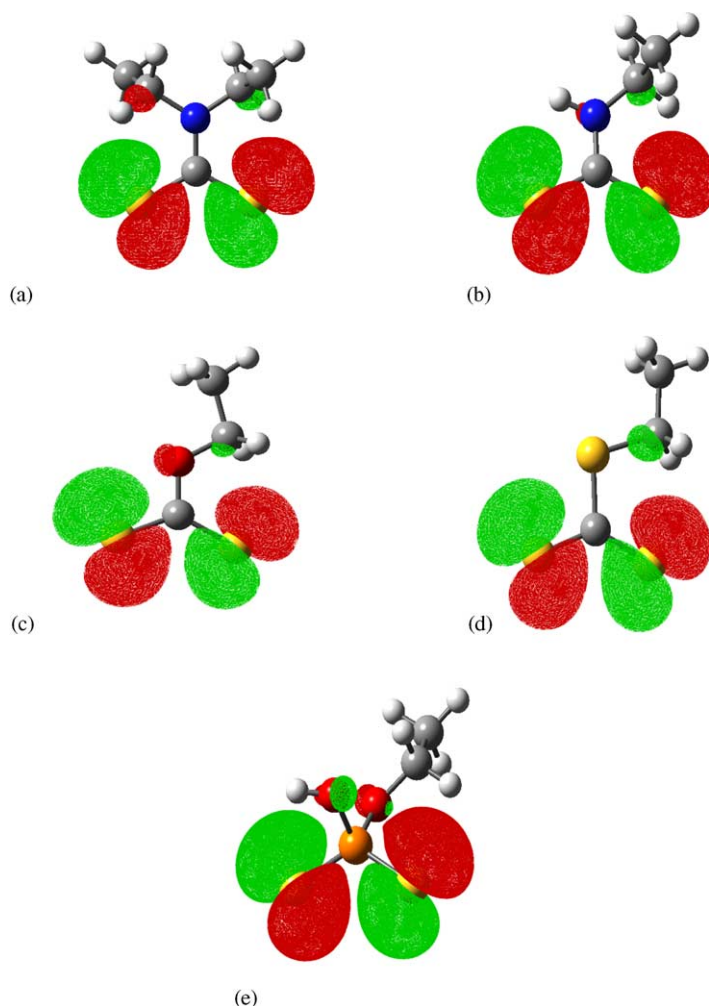


Fig. 4. Frontier HOMOs for the collector ions at an isosurface value of 0.035 au (B3LYP/3-21G\*). (a) Diethyl dithiocarbamate; (b) ethyl dithiocarbamate; (c) ethyl dithiocarbonate (xanthate); (d) ethyl trithiocarbonate; (e) ethyl dithiophosphate.

The HOMO representations of the collector ions are presented in Fig. 4. We considered HOMO orbitals, because the collectors examined in this study act as electron donor and give up their electrons from HOMO to the Ag (+1) d orbitals of corresponding symmetry. As it is seen in Fig. 4, HOMO orbitals are mostly localized to the sulfur atoms, which is the chelating part of them. For this reason, we have to expect the bond formation to occur at this site. It should be noted that collector ions seem to be sensitive to the HOMO energies; and going from ethyl dithiophosphate ion to diethyl dithiocarbamate, the energies of the HOMOs are raised (see Table 3). This is the cause of the increased activity of the collector ions to Ag (+1) ion. Using the HOMO and  $\Delta E$  energies, the reactivity order of the collectors is found as  $(C_2H_5)_2NCS_2^- > C_2H_5NHCS_2^- > C_2H_5OCS_2^- > C_2H_5SCS_2^- > (C_2H_5O)(OH)PS_2^-$ . Additionally, the energy order of the HOMOs is not changed with the improvement of the basis set quality to the 6-31++G\*\* level. Consequently, using dialkyl dithiocarbamate for the flotation of acanthite mineral will meet the preconditions of the flotation process with better floatability comparing to the other thiol collectors studied.

#### 4. Conclusions

In this study, the interactions of the thiol collectors with Ag (+1) were modeled. The outcome of these calculations showed that dithiocarbamate ions could be used as the most effective collectors in the flotation of the sulfide minerals.

The partial atomic charges evaluated from Mulliken population analysis and CHelpG methods do not provide satisfactory description of the chemical activity of the thiol collectors. A relationship was found between the HOMO energies of the collector ions and the interaction energies with the Ag (+1) ion. The results showed that HOMO energies could be used as a reactivity descriptor for the selected collectors. The interaction energies may be overestimated due to the difficulties in the modeling of the system. However, the theoretical calculations permit us to understand the role of these collector molecules in the initial adsorption step of the flotation processes for acanthite and other sulfide minerals.

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