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R. N. AZHIGULOVA, R. A. OMAROVA, A. A. BATYRBAEVA,
A. A. ARYSTANBEKOV, M. T. OSHAKBAEV

Al-Farabi Kazakh National University, Almaty, Republic of Kazakhstan,
A. Bekturov Institute of Chemical Sciences, Almaty, Republic of Kazakhstan

QUANTUM CHEMICAL MODELING OF ADSORPTION PROCESS AT FLOTATION ON THE CLUSTER OF SPHALERITE AND WURTZITE

Abstract. A quantum-chemical calculation of the behavior of molecule on the surface of sphalerite and wurtzite is carried out using the views of Density Functional Theory (DFT). Energy minima are determined from the geometric coordinates of the molecule corresponding to the ground and metastable states, clusters of sulfide minerals of sphalerite and wurtzite are constructed. An orbital analysis of the studying system has been carried out, and the orbitals have been restructured during the interaction of this system.

Key words: cluster, sulphide, minerals, sphalerite, wurtzite, Density Functional Theory molecular modeling.

The models of estimation the interaction of mineral-sulfides system using quantum-chemical methods have become widespread. The essence of such studies is that the very difficult problem of interaction with the surface of solid reduces to the calculation of simple models which reflect the basic properties of the complex. Well known, the two types of model approaches are most widely used: solid-body models which take into account the "collective" properties of solid, and molecular models that take into account only a part of the solid (cluster). At present time the latter method have been widely used in the quantum-chemical investigation processes. It should be noted that the role of molecular modeling in chemistry is quite large, despite the obvious priority of experimental research in this field of natural science. The most significant are theoretical results that are impossible, extremely difficult or too expensive to obtain by experimental means [1, 2]. Traditionally, modeling tasks include the definition of the structure of individual molecules, molecular associates or fragments of solids, as well as the description of the mechanisms of chemical reactions at the molecular level. Such modeling is most often in recent years carried out using the methods of quantum chemistry.

The attractiveness of molecular models to estimate the reactivity of minerals-sulfides with respect to a certain reagent consists in the possibility of taking into account the structural-geometric and chemical heterogeneity of the surface of solid. In this case, the establishment of correlation with the experimental data is great importance for evaluating the correctness of the calculations. The results of the experimental study are also very important, when choosing the initial model [1-3].

For calculations, two fairly simple clusters were taken: Zn_4S_4 for sphalerite and Zn_6S_6 for wurtzite. The results of calculations of bond lengths and a number of energy characteristics for less complex clusters of sulfide minerals are presented in table 1, figures 1 and 2 show geometric models of two simple clusters of sphalerite and wurtzite.

Table 1 – Geometric, electronic characteristics and enthalpy of formation of sphalerite and wurtzite clusters

Compound, composing elements	q, units of charge	r, nm	$\Delta_f H$, kJ/mol	Ionization potential, eV	μ, D	E_{HOMO}, eV	E_{LUMO}, eV
Sphalerite S Zn Zn - S	 -0,001 +0,001	 0,24	-1244,36	11,04	0	-11,04	-3,08
Wurtzite S Zn Zn – S	 -0,12 +0,12	 0,23	-2112,13	10,36	0,001	-10,36	-5,04

Table 1 shows that in the model clusters of sphalerite and wurtzite, the Zn-S bond length is 0.241 nm and 0.231 nm, respectively. The latter shows that an increase in the number of atoms in the model cluster leads to a certain reduction in the length of the Zn-S bond.

In all the models studied, the positive charge is concentrated on the metal atoms, and the negative charge on the sulfur atoms. The electron density in all clusters is higher for the more electronegative sulfur atom.

All clusters taken for study are thermodynamically stable, since they are characterized by negative values of enthalpy of formation. The enthalpy of formation, in addition, is the energy characteristic of bonds in clusters. Proceeding from this, a comparison of this characteristic for clusters of the same type of zinc sulfides indicates a large thermodynamic stability of the wurtzite cluster.

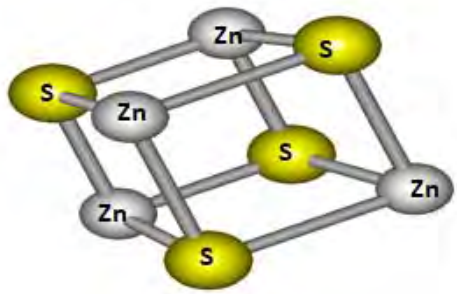

Figure 1 – Geometric model of sphalerite cluster Zn_4S_4

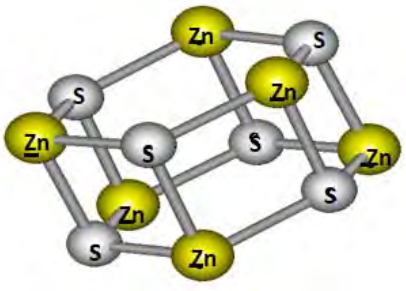

Figure 2 – Geometric model of the wurtzite cluster Zn_6S_6

The ionization potentials determined for all the clusters were in the range about 12.19-10.36 eV (in absolute value). The presence of atoms identical in electronegativity in clusters of sphalerite and wurtzite leads to approximately the same ionization potentials. According to this the energies of the higher occupied molecular orbitals (HOMO) for these clusters are approximately equal. The energies of the lowest unfilled molecular orbital(LUMO) in all clusters differ more appreciably: the LUMO energy, which is the largest in absolute value, is characteristic for the wurtzite cluster, and the smallest for the sphalerite cluster.

The considered sphalerite clusters Zn_4S_4 and wurtzite Zn_6S_6 have a sufficiently large difference between the energies of the boundary orbitals, i.e. upper occupied (HOMO) and lower free (LUMO) molecular orbitals. This indicates that in the clusters studied the polar covalentbond, and the clusters of iron and lead sulfides are coordinating unsaturated, which indicates their potential to form various bonds with flotation agents.

A rather interesting picture is revealed when considering the dipole moments of the clusters studied. In particular, a comparison of this characteristic for pyrite and sphalerite clusters containing the same number of atoms in their composition shows that in the first of them the dipole moment is 0.011 D, while in the second one it is absent. The dipole cluster of a wurtzite containing the same atoms as the sphalerite cluster is insignificant and equal to 0.001 D. In general, it can be noted that the dipole moments of the sphalerite and wurtzite clusters have relatively small values, which indicates a high symmetry of both models. The sphalerite cluster is completely symmetrical. Confirmation of these conclusions is the charge characteristic in all model clusters.

Thus, as a result of approbation of the semiempirical “DFT” method, the parameters described abovefor the clusters oftwo zinc sulfides are calculated for the first time.

In the flotation pulp molecules and ions of different nature can exist, and they can participate in adsorption processes on the surfaces of sulfide minerals. Therefore, first of all we carried out a quantum chemical study of the sphalerite and wurtzite model complexes with the neutral molecules of mineral acids, water and hydrogen peroxide. The model complexes of sphalerite and wurtzite for study were $Zn_4S_4{\cdot}HF$, $Zn_4S_4{\cdot}HCl$, $Zn_4S_4{\cdot}HBr$, $Zn_4S_4{\cdot}H_2O$, $Zn_4S_4{\cdot}H_2O_2$, $Zn_4S_4{\cdot}HNO_2$, $Zn_4S_4{\cdot}HClO_2$and $Zn_6S_6{\cdot}HF$, $Zn_6S_6{\cdot}HCl$, $Zn_6S_6{\cdot}HBr$, $Zn_6S_6{\cdot}H_2O$, $Zn_6S_6{\cdot}H_2O_2$, $Zn_6S_6{\cdot}HNO_2$, $Zn_6S_6{\cdot}HClO_2$respectively.

The results of the calculation represented in tables 2 and 3.

The cluster systems:mineral-neutral molecules. In table 2 represented models of the adsorption complex of sphalerite cluster with various molecule of some inorganic substances. Some of the results published in [6].

The binding energy or energy of the adsorption $\Delta_{adc}E$ can be defined as

$$\Delta_{adc}E = E_{adc} - \left(E_T + \sum_i E_{a,i} \right),$$

where E_{adc}, E_T and E_a are the total energies of the adsorption complex of the sulfide mineral cluster and the adsorbate respectively [4-6].

Table 2 – Charge characteristics (q, charge units), bond lengths (r_{A-B}, nm), enthalpy of formation ($\Delta_f H^o$, kJ/mol), total energy ($E_{tot,}$ kJ/mol), dipole moment (μ, D) in model systems sphalerite-neutral molecules

Compound	q, units charge	r_{A-B}, nm	$\Delta_f H^o$, kJ/mol	μ, D
Zn_4S_4·HF Zn (on all atoms) S_3, S_4, S_6 S_9 F	 -0,01 +0,02 -0,003 -0,17	 Zn_7-S_9 0,241 F_9-H_{10} 0,094 S_9-H_{10} 0,409	-1507,41	1,63
Zn_4S_4·HCl Zn S_1, S_3 S_5, S_7 Cl	 -0,01 +0,03 -0,03 -0,20	 S_8-H_9 0,550 H_9-Cl_9 0,134 Cl_{10}-Zn 0,241	-1343,36	2,79
Zn_4S_4·HBr Zn S_3 S_4, S_7, S_8 Br	 -0,002 +0,01 +0,03 -0,30	 S_3-H_{10} 0,170 Br_9-H_{10} 0,156 S_3-Zn_5 0,241	-1272,48	4,15
Zn_4S_4·H_2O Zn S_3, S_2 S_7 S_8 O_{10}	 -0,01 +0,01 -0,003 0,02 -0,36	 S_7-H_9 0,409 H_9-O_{10} 0,095 O_{10}-H_{11} 0,095 S_7-Zn_6 0,232	-1468,12	1,92
Zn_4S_4·H_2O_2 Zn S_2, S_4, S_6 S_8 O_{10}, O_{11}	 -0,01 +0,02 -0,003 -0,21	S_8-Zn_6 0,241 S_8-H_9 0,408 H_9-O_{10} 0,094 O_{10}-O_{11} 0,148 O_{11}-H_{12} 0,094	-1414,69	0,15
Zn_4S_4·HNO_2 Zn S_1, S_4, S_8 S_5 N_{11} O_{10} O_{12}	 -0,01 +0,02 -0,01 +1,36 -0,46 -0,55	 S_8-H_9 0,757 H_9-O_{10} 0,285 O_{10}-N_{11} 0,138 N_{11}-O_{12} 0,117 S_8-Zn_6 0,241	-1307,00	2,40
Zn_4S_4·$HClO_2$ Zn S_2 S_3,S_6, S_7 O_{11} Cl_1	 -0,11 +0,10 +0,12 -0,32 +0,12	 Cl_1-O_{11} 0,171 O_{11}-H_{10} 0,095 H_{14}-S_6 0,596 S_6-Zn 0,231	-2255,01	1,78

In table 3 represented data about adsorption energies in sphalerite cluster with molecules of some inorganic acids, water and hydrogen peroxide.

Table 3 – Adsorption energies in sphalerite cluster systems - reagent molecules

Adsorption system	ΔE_{adc}, kJ/mol
HF	-142.13
HCl	-156.24
HBr	-157.23
H_2O	-135.12
H_2O_2	-127.26
HNO_2	-21.14
$HClO_2$	-367.19

Table 3 shows that the adsorption systems of sphalerite clusters with simple molecules have negative adsorption energies that are negative in sign and average in absolute value. By changing the absolute values of the adsorption energy in the case of molecules of mineral acids, water, and hydrogen peroxide, a series can be made:

$$HClO_2 > HBr \approx HCl > HF > H_2O > H_2O_2 > HNO_2.$$

The minima energy of adsorption has HNO_2 which equal -21.14 kJ/mol and maxima energy has $HClO_2$ about -367.19 kJ/mol. The calculated adsorption energy allows a preliminary conclusion about the strength of the interaction of clusters and allows you to choose substances for flotation

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Резюме

Р. Н. Ажигулова, Р. А. Омарова, А. А. Батырбаева,
А. Арыстанбеков, М. Т. Ошакбаев

КВАНТОВО-ХИМИЧЕСКОЕ МОДЕЛИРОВАНИЕ ПРОЦЕССОВ АДСОРБЦИИ В СИСТЕМАХ КЛАСТЕР СФАЛЕРИТА И ВЮРЦИТА-МОЛЕКУЛЫ ФЛОТОРЕАГЕНТОВ

Квантово-химическим расчетным методом исследовано геометрическое и электронное строение некоторых окислителей, наиболее часто присутствующих в реакционной среде флотационной пульпы. Установлена закономерность изменения величин потенциала ионизации, на основании которой сделан вывод о реакционной способности исследованных молекул.

Ключевые слова: сульфидные минералы, сфалерит, вюрцит, молекулярное моделирование.

Резюме

Р. Н. Ажигулова, Р. А. Омарова, А. А. Батырбаева,
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СФАЛЕРИТ ЖӘНЕ ВЮРЦИТ КЛАСТЕРІ-ФЛОТАРЕАГЕНТЕРДІҢ МОЛЕКУЛАЛАРЫ ЖҮЙЕЛЕРІНДЕГІ АДСОРБЦИЯЛЫҚ ПРОЦЕСТЕРДІ КВАНТТЫҚ-ХИМИЯЛЫҚ МОДЕЛЬДЕУ

Флотациялық пульпадағы реакциялық ортада жиі кездесетін кейбір тотықтырғыштардың геометриялық және электрондық құрылымдары кванттық химиялық есептеу әдісімен зерттелген. Потенциал ионизацияның шамаларының өзгеру заңдылықтары анықталды, оның негізінде зерттелген молекулалардың реакциялық қабілеттіліктеріне қорытынды жасалды.

Түйін сөздер: сульфидті минералдар, сфалерит, вюрцит, тотықтырғыш, молекулалық модельдеу.