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АНАЛИЗ ВЗАИМОДЕЙСТВИЯ ЧЕТЫРЕХАТОМНОГО КЛАСТЕРА СЕРЕБРА С ПОВЕРХНОСТЬЮ ДИОКСИДА КРЕМНИЯ МЕТОДАМИ ТЕОРИИ ФУНКЦИОНАЛА ПЛОТНОСТИ

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Ключевые слова: теория функционала плотности, DGDZVP, диоксид кремния,   металлическое серебро, натуральные орбитали связи.

Аннотация. Проведены расчеты некоторых серебро- и кремний содержащих молекул в газовой фазе методом функционала плотности с использованием полноэлектронного базисного набора DGDZVP в программном пакете GAUSSIAN'03 и TZ2P+ в программе Амстердамский функционал плотности. Показано, что диоксид кремния с большой вероятностью может взаимодействовать с кластером серебра. Рассчитанные рентгеноэлектронные уровни натуральных орбиталей связи указывают на существенное взаимодействие между разрыхляющими орбиталями атомов серебра.

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ANALYSIS OF THE INTERACTION OF FOUR-ATOM SILVER CLUSTER WITH SURFACE OF SILICON DIOXIDE BY DENSITY FUNCTIONAL THEORY METHODS

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Abstract. The calculations of some silver- and silicon -containing molecules in the gas phase at the density functional method with using all-electron DGDZVP basis set in GAUSSIAN'03 software package and TZ2P+ basis set in Amsterdam density functional. It is shown that the silicon dioxide with a high probability can interact with the silver cluster. The calculated ESCA levels and natural orbital bond point to a significant interaction between the antibonding orbital of silver atoms.

Introduction. Composite materials consisting of silicon dioxide and deposited on its surface particles, clusters and ions of silver are actively researched for use as catalysts in CO afterburning effectively employed in low-temperature region and selective with respect to CO and hydrogen [1].

At present, it is known that the activity of these catalysts determined by the size of the silver particles [2] and the surface composition of the support [3] and the presence of redox-rehabilitation treatments [4].

Previously it has been suggested [5], that in the process of the latter, along with the silver particle redispersion [6], the interface layer is formed, which plays a role in the formation of active centers. So the study of the interaction of oxidized and reduced silver particles with a silicon dioxide surface defect quite true.

One of the most sensitive methods in this area is the X-ray photoelectron spectroscopy, and the fact of the presence of the interface layer was found with its help [5].

However, the small magnitude of the contribution of this layer to the overall signal generated by the photo-electron beam does not mainly from silver coated surface of the carrier and the array of silver particles on the surface does not permit reliable conclusions on its composition and electronic state of silver. Earlier calculations have been carried out for uncharged particles and silver clusters Ag_n (n = 1-4), interacting с unbridged oxygen penny-set ($\equiv$Si-O·, NBO-defects), as well as dangling bonds $\equiv$Si·dehydroxylated surface of SiO_2.

In [7, 8] was concluded that the interaction of silver with clusters $\equiv$Si· there is a charge transfer in the cluster with the silicon atom, and a defect NBO - clusters on the oxide support. The energies of adsorption of silver clusters on the defects of silicon dioxide are calculated.

It was shown that surface defects can act as a trap of adsorbed silver atoms, diffusion preventing their surface, which is important for the interface layer, the nucleation of silver particles and possibly functioning of active centers.

In addition, in [9] it was calculated the interaction of copper clusters, which properties are quite close to the properties of silver, with a regular surface of silica and neutral oxygen vacancies ($\equiv$Si-Si$\equiv$). It is shown that the active surface is not regular in relation to the copper clusters, and the activity decreases in the number of defects NBO> $\equiv$Si > $\equiv$Si-Si$\equiv$.

In [10] it is shown that the interaction of copper clusters with NBO-defect a significant shift due 2p-energy level of silicon about 0.6-1 eV is observed only at a small cluster size. For large copper clusters shift does not exceed 0.1 eV.

In [11] it was performed quantum chemical calculations of silver clusters models on hydroxylated silica surface in the oxidized and reduced forms and electronic spectra. In this case the calculated and experimental spectra containing silver in an oxidized form good matched. However, the calculation of the energy of interaction between oxidized forms of silver and surface defects in this work was not carried out.

In [12] it was first noted that the oxygen atoms of the silanol groups of silica involved in the formation of the intermediate in the oxidation of CO on platinum particles, and the hydrogen formed during the decay of the intermediate with platinum particles and is held constantly returned to the system.

Quantum-chemical modeling of reversible spillover hydrogen on zeolite-OH groups on the metal clusters, rhodium, iridium and gold deposited on the zeolite hydroxylated performed in [13].

One way to study the interactions between the silver clusters and the surface of the silicon dioxide are theoretical quantum chemical calculations using theory methods density functional (DFT).

Using a sufficiently accurate functional and basis set allows to receive adequate values of the physical parameters required. To investigate the above-mentioned features of these interactions can be used cluster models. Small cluster models have shown to be useful in the study of the adsorption of the individual components and provide a fairly accurate description of adsorbed structures, vibrations and energies of the physical and chemical adsorption [14-17].

Using DFT methods, the optimized structure of the four-atomic silver clusters, often used for the calculations, is essentially planar and rhombic

A number of researchers [18-20] have shown that the most optimal in terms of time and computer resources, methods to DFT calculations of systems containing atoms of elements of the fifth period (including silver), is a combination of three-parameter hybrid functional B3LYP with full-valence-split basis with the addition of polarization functions DGDZVP. This basic set of specially optimized for DFT calculations of compounds with heavy atoms.

In this article, we attempt to computer modeling of the interaction between the atomic and cluster silver and hydroxylated surface of silica, obtained structural, spectral and energy parameters of the complexes.

Experimental part. Calculations were performed using a standard software package GAUSSIAN 03 [21]. In order to optimize the geometry of the studied clusters it was used full-DGDZVP basis set,

designed specifically for the settlement of the density of the theory [22]. Calculations performed by the B3LYP hybrid density functional B3 exchange functional Becke [23] and functional correlation Lee, Yang and Parr (LYP) [24]. Currently, this method is generally accepted to describe the thermodynamic characteristics and the best agreement with the experimental values [25].
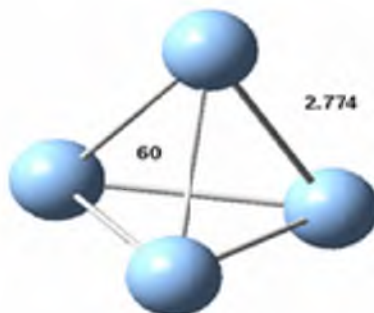

Fig. 1 – Optimized structure of silver cluster at B3LYP/DGDZVP level

The geometrical parameters of designed molecules and clusters are fully optimized; no imaginary vibrational frequencies confirmed their stationary character. Initial state of silver was a cluster in which atoms are arranged at the vertices of a tetrahedron (Fig. 1).

Dissociation energies of calculated compounds have been adjusted to reflect a zero vibrational energy (ZPVE) and reduced to standard conditions (298.15K, 1 atm) using thermal corrections to the enthalpy and free energy.

To describe the nature of the chemical bond approach utilized natural orbitals bond [26]. On the other hand, these compounds also have been studied using a program ADF (Amsterdam density functional theory) [27].

We used functional OPTX exchange [28], combined with PBE correlation functional [29] with the irreducible Slater triple dzeta + polarization basis set using the frozen-core approximation to the inner electrons.

Relativistic effects of heavy atoms have been accounted for using the regular zero-order approximation (ZORA) [30], which gives more realistic results than the widely used Pauli formalism in the Gaussian package. The effective charges on the atoms were evaluated in approximations Mulliken, Hirsch, Voronoy and multidipole charge analysis [27].

Results and its discussion

To assess the "quality" of the calculations it is necessary to rely on some physical and chemical properties of these compounds, which are known sufficiently accurate experimental values. In the past we used as bond lengths, the frequency of stretching and deformation vibrations in the IR spectra and dissociation energies of some simple silver and silicon compounds.

$$R(exp.) = 0.13 + 0.903R(cal.) \qquad r = 0.998; \; s = 0.03; \; n = 12 \qquad (1)$$

In these and the following regression equations r - is the coefficient of correlation, s - standard deviation, and n - number of compounds included in the correlation. It should be noted that the silver diatomic molecules, silicon diatomic, trihydric and pentahydric compounds have been calculated.

A similar dependence was obtained somewhat well in the calculation of the same molecules in the program of the ADF (Figure 2b.):

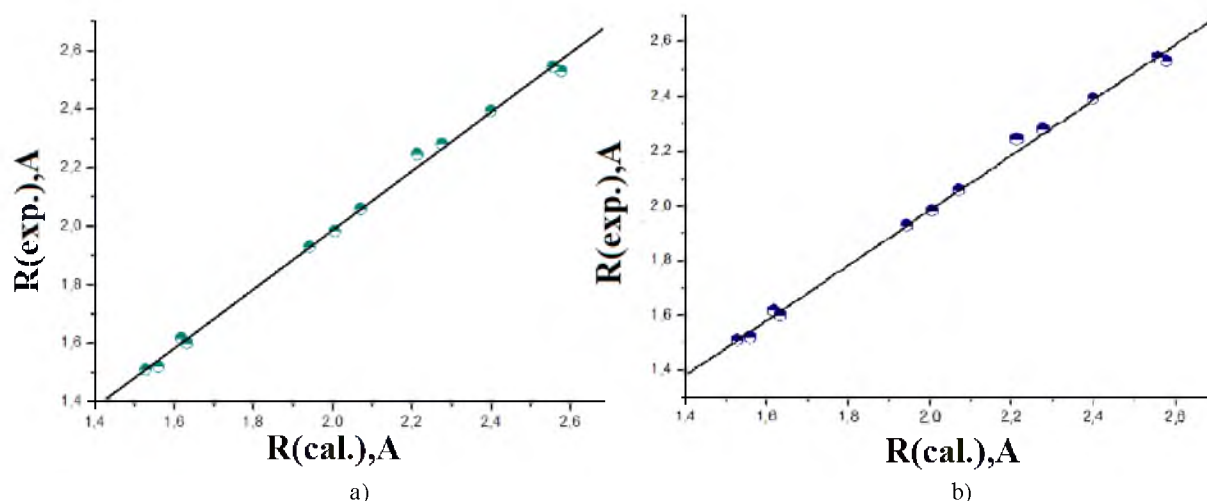$$R(exp.) = -0.03 + 1.01R(cal.) \qquad r = 0.999; \; s = 0.02; \; n = 12 \qquad (2)$$

Fig. 2 – The relationship between the calculated and experimental bond lengths in certain compounds
of silver and silicon in the approximation B3LYP / DGDZVP (a) and BP86TZ2P + (b)

Fig. 2a shows the correlation between the experimental [31] and calculated by B3LYP / DGDZVP
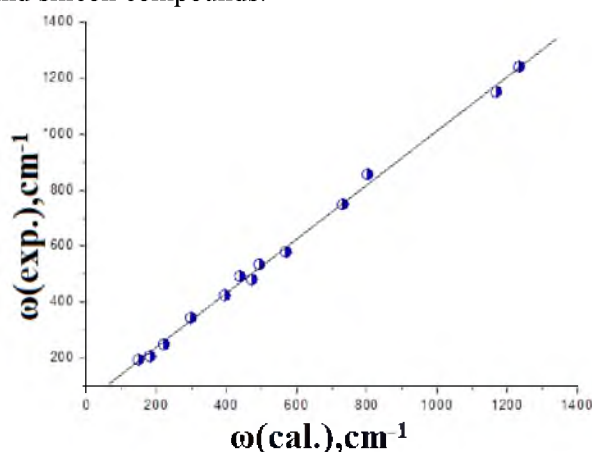bond lengths for some silver and silicon compounds:

Fig. 3 – The relationship between the experimental and calculated vibrational frequencies in the IR spectrum of some silver
and silicon compounds at B3LYP DGDZVP

Fig. 3 shows the linear correlation between the calculated at Gaussian program and experimental
values of the frequencies of the stretching and bending vibrations in the IR spectra of some silver and
silicon compounds [32] fine quality, which indicates that calculations correctly describe the vibrational
transitions.

$$\omega(exp.) = 45.8 + 0.97\omega(cal.) \quad r = 0.999; \, s = 18; \, n = 13 \tag{3}$$

The good correlations between experimental and calculated bond lengths and vibrational frequencies,
and the coefficients of R (cal.) close to the unit, indicate a high reliability level used in the calculations.

The optimized structure of silver nitrides and silicon halides, hydrides, has allowed them to calculate
the dissociation energy of both the used calculation methods: Gaussian (4) and ADF (5) (Figure 4a, b.).

$$De(exp.) = 113 + 0.55De(cal.) \qquad r = 0.986; \, s = 26; \, n = 17 \tag{4}$$

$$De(exp.) = 59 + 0.63De(cal.) \qquad r = 0.986; \, s = 26; \, n = 17 \tag{5}$$

The same correlation coefficients and standard deviations of both correlation equations show that the
two methods of density functional theory can be obtained sufficiently reliable thermodynamic parameters.
Besides this calculation of electronic absorption spectrum of Ag_4Si (OH_3) O^+ system by
B3LYP/DGDZVP (291 and 387 nm) and BP86TZ2P+ (298 and 360 nm) methods indicates a good

agreement with the experimental spectrum (294, 374-392 nm) [11].

Fig. 5 presents the optimized structure of the for-atom clusters of silver complex and silica on both levels of the theory.

It was established that the silver cluster has a tetrahedral structure. The length of the connection between adjacent atoms of Ag was 2.774 Å for values tetrahedral bond angles of 60°.

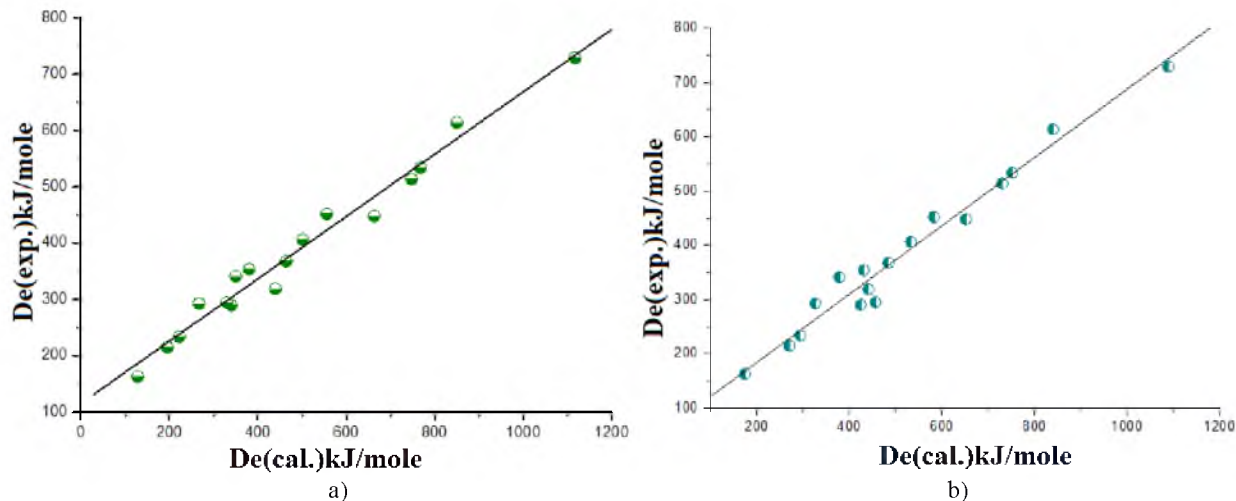a)   b)

Fig. 4 – The relationship between the experimental and computational B3LYP/ DGDZVP (a) and BP86TZ2P + (b) methods of the dissociation energies of some silver and silicon compounds
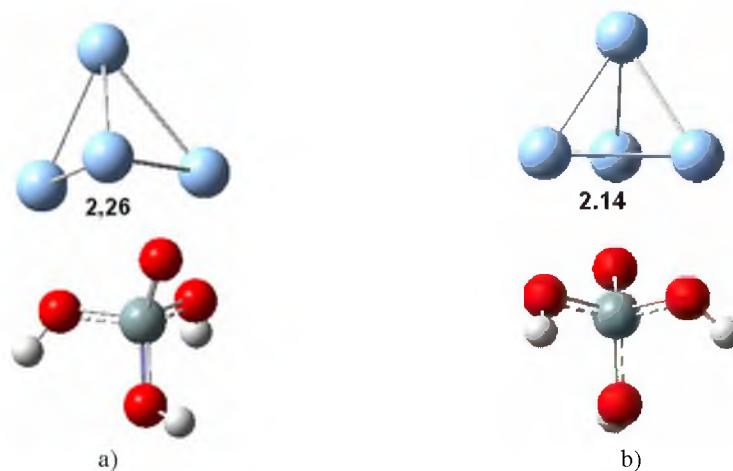

a)   b)

Fig. 5 – Optimized structure Ag$_4$Si (OH)$_3$O+ B3LYP/DGDZVP (a) and BP86TZ2P+ (b) approximation

The resulting optimized bond length Ag-Ag are in agreement with the experimental and calculated results (for example, Ag-Ag distance of 2.889 Å [33], 2.838 Å [15], 2.66 Å [16]).

Some differences in the geometric parameters can be explained by a single positive charge used in this paper silver cluster.

When interacting with the silica surface of the bond lengths Ag-Ag increase somewhat and become unequal from 2.86 to 3.01 Å, and the distance from the nearest atom of silver to the coordinated oxygen atom is equal to 2.262 and 2.140 Å in different approximation that only a little more of the covalent bond length AgO (2.097 Å).

Changes in bond lengths Ag-Ag reflected in the internal energy levels Ag3d (Table. 1), which decreases with the coordination of the calculation of the two methods. This indicates the transfer of the electron density to the silver cluster.

Table 1 – Calculated internal energy levels (eV) in the approximations of natural orbitals (nbo),
Mulliken (Mull) in the Gaussian programs and ADF (adf)

System	E_{Ag}(nbo)	EAg(Mull)	EAg(adf)	ESi(nbo)	ESi(Mull)	ESi(adf)
Ag_4^+	376.2	376.4	365.7			
$Si(OH)_3O$				101.4	101.6	96.2
$Ag_4Si(OH)_3O^+$	375.4	375.6	365.5	103.9	104.1	98.5

Comparison between the calculated and experimental level values obtained by ESXA [34] (368 eV) leads to good agreement between them (1-3%) for silver clusters. Si2p energy level under the coordination increases in all approximations, which indicates the shift of the electron density from the silicon atoms in the coordination.

The redistribution of the electron density on the atoms on the basis of various approximations is given in Table. 2. It can be seen that regardless of the approach used in the evaluation of effective charges on the atoms, in coordination decreases the electron density on the atoms of silver and silicon.

Table 2 – Change in electron density at one atom in $Ag_4Si(OH)_3O+$, calculated by the B3LYP/DGDZVP (a) and BP86/TZ2P+ (b)

Atom	ΔqMulliken (a)	ΔNBO (a)	ΔqMulliken (б)	ΔqHirsh (б)	ΔqVoronoy (б)
Ag	-0.121	-0.187	-0.114	-0.078	-0.068
О(коорд.)	0.422	0.740	0.301	0.172	0.222
Si	-0.119	-0.075	-0.005	-0.059	-0.003
O	0.082	0.044	0.065	0.025	0.026

The sign (-) corresponds to the decrease in the electron density

In the oxygen atom directly coordinating with silver clusters, the electron density increases significantly. Minimal increase in the electron density occurs at the oxygen atoms of the remaining OH groups. Apparently serves as a coordinating "bridge" oxygen atom for the transfer of electron density from the silver cluster and a central silicon atom to oxygen atoms.

A similar pattern was observed for the previously non-transition elements complexes with organic ligands [35]. From the point of view of the natural orbitals method of chemical bonding connection between the cluster of silver and silica is carried out by interaction between the anti-bonding silver lone electron pairs between its (Table 3).

This is also evidenced by the appearance of molecular occupied orbitals (HOMO) and lowest unoccupied (LUMO) (Fig. 6).
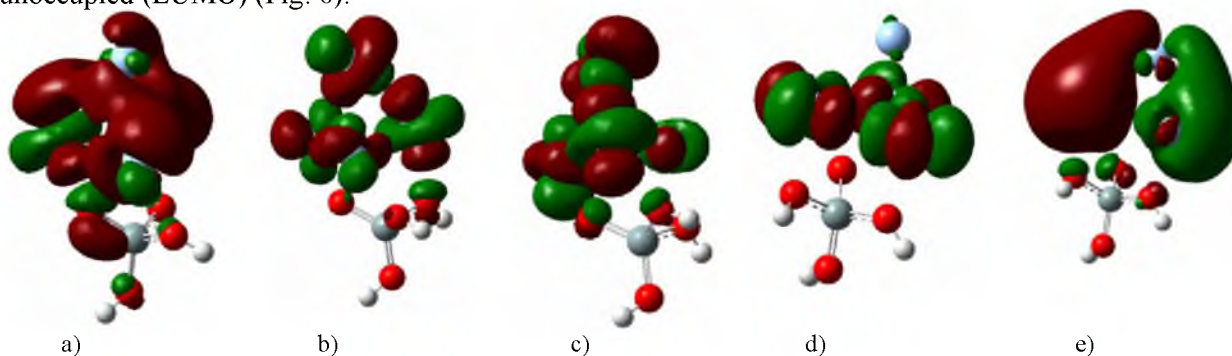

a)   b)   c)   d)   e)

Fig. 6. Molecular orbitals of the $Ag_4Si (OH)_3O^+$ complex: В3МО (a),
В3МО-1 (b), В3МО-2 (c), В3МО-3 (d), НСМО (e)

The electron density in the HOMO of (a-d) and LUMO (e) belongs to the cluster mainly silver, it confirms that such interactions.

If the cluster Ag_4^+ silver along with five electron lone pairs of d-type for each atom, there is only one pair of electrons anti-bonding s-type, in coordination appear four s-antibonding electron lone pairs of with an average population of 0.384e.

Table 3 – Analysis of donor-acceptor interaction of $Ag_4Si(OH)_3O^+$ system on the basis of the natural bond orbitals B3LYP/DGDZVP method

Orbital	Atom	Population, e	Hybridization	Interaction Between orbitals	The interaction energy, kcal/mol
$\sigma(O_5\text{-Si})$	O Si	1.982	$sp^{1.47}$ $sp^{2.40}$	$LP^*(Ag_1){\rightarrow}LP^*(Ag_2)$	105
$\sigma(O_7\text{-Si})$	O Si	1.986	$sp^{1.77}$ $sp^{2.63}$	$LP^*(Ag_1){\rightarrow}LP^*(Ag_3)$	50
$\sigma(O_9\text{-Si})$	O Si	1.984	$sp^{1.72}$ $sp^{3.43}$	$LP^*(Ag_4){\rightarrow}LP^*(Ag_1)$	162
$\sigma(O_{11}\text{-Si})$	O Si	1.984	$sp^{1.73}$ $sp^{3.25}$	$LP^*(Ag_4){\rightarrow}LP^*(Ag_2)$	85
LP(Ag)	Ag	1.998	d		
LP*(Ag)	Ag	0.384	s		

It can be assumed, primarily on the basis of the reduction of internal energy levels Ag3d, that the coordination of the silver cluster it is certainly involved in the complex formation, but the electronic density of the substrate goes to antibonding orbitals, and does not affect the effective charges of the silver atoms.

In addition, a sufficient strength of the interaction between the cluster and silver silica indicate the thermodynamic parameters of the reaction, according to which the change of the Gibbs energy of -44 kcal/mol, and the change in the interaction energies calculated by ADF equals -65 kcal/mol, which is close enough to [36].

Conclusions. It is shown that the method used for calculating the density functional theory within GAUSSIAN and Amsterdam density functional program gives adequate results in predicting the geometric parameters, the IR spectra and dissociation energies of silver and silicon compounds.

1. The analysis of the bonding in $Ag_4Si(OH)_3O^+$ structure by the method of natural bond orbitals. It is shown that the formation of the connection between the cluster of silver and the substrate is determined by the interaction between a anti-bonding orbitals of silver atoms.

2. The possibility of a strong interaction between the surfaces of the silica with silver cluster was shown. The ESCA levels and thermodynamic parameters were calculated.

<div align="center">REFERENCES</div>

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ТЫҒЫЗДЫҚ ФУНКЦИОНАЛЫ ТЕОРИЯСЫ ӘДІСТЕРІМЕН КҮМІСТІҢ ТОРТ АТОМДЫ КЛАСТЕРІНІҢ КРЕМНИЙ ДИОКСИДІНІҢ БЕТІМЕН ОЗАРА ӘСЕРІН ТАЛДАУ

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Түйін сөздер: тығыздық функционалы теориясы, DGDZVP, кремний диоксиді, металл күміс, байланыстың табиғи орбитальдары.

Аннотация. Амстердам тығыздық функционалы бағдарламасындагы GAUSSIAN'03 және TZ2P+ бағдарламалық пакетіндегі DGDZVP толық электронды базисті жиынын пайдаланып тығыздық функционалы әдісімен газдық фазадагы кейбір күміс- және кремний құрамдас молекулаларының есептеулері жүргізілді. Кремний диоксиді үлкен ықтималдықпен күміс кластерімен әсерлесетіндігі көрсетілген. Есептелген байланыстың табиғи орбитальдарының рентгеноэлектрондық деңгейлері күміс атомдарындагы ыдырату орбитальдарының арасында едәуір әрекеттесу бар екендігін көрсетті.