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АНАЛИЗ ВЗАИМОДЕЙСТВИЯ ПОВЕРХНОСТИ МЕТАЛЛИЧЕСКОЙ
РТУТИ С АММОНИЙНЫМИ ОСНОВАНИЯМИ НА ОСНОВАНИИ
ТЕОРИИ ФУНКЦИОНАЛА ПЛОТНОСТИО. Х. Полешчук¹, С. В. Ковалева², М.Н. Ермаханов³,
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Ключевые слова: теория функционала плотности, псевдопотенциал, аммонийные основания, металлическая ртуть, натуральные орбитали связи.

Аннотация. Проведены расчеты некоторых ртутьсодержащих молекул в газовой фазе на основании расчетов методом функционала плотности с использованием псевдопотенциального базисного набора для атома ртути и 6-311+G(d,p) для других атомов в программном пакете *GAUSSIAN 03* и *TZ2P+* в программе Амстердамский функционал плотности. Показано, что катион аммония по сравнению с радикалом аммония с большей вероятностью может взаимодействовать с поверхностью металлической ртути. Рассчитанные термодинамические параметры указывают на невозможность взаимодействия с поверхностью металлической ртути таких аминов, как гидроксилламин, гидразин и тетраметиламин.

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USING OF DENSITY FUNCTIONAL THEORY FOR ANALYSIS
OF SURFACE INTERACTION BETWEEN METALLIC MERCURY
AND AMMONIUM BASESO. Kh. Poleshchuk¹, S.V. Kovaleva², M.N. Ermakhanov³,
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Key words: density functional theory, pseudopotential, ammonium bases, metallic mercury, natural bond orbital.

Abstract. The calculations of some mercury-containing molecules in the gas phase on the basis of calculations by the density functional method with use of the pseudopotential basis set for mercury atom and 6-311+G(d,p) for other atoms in the software package *GAUSSIAN'03* and *TZ2P+* in the Amsterdam density functional program were implemented. It is shown that the ammonium cation in comparison with the ammonium radical is more likely to interact with the surface of the metallic mercury. The calculated thermodynamic parameters indicate the inability of amines such as hydroxylamine, hydrazine and tetramethylamine to interact with the surface of metallic mercury.

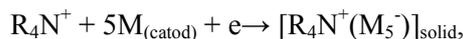
Introduction. Pseudo metal amalgams, which include amalgams of ammonia, pyrrolidine and their derivatives represent of great interest. The most studied is an amalgam of ammonium, which was first

obtained by electrolysis of ammonium carbonate solution on mercury cathode, as well as a result of the exchange reaction of ammonium salts with alkali metal amalgam.

Generalization of the works on the preparation and the study of physical and chemical properties of ammonium amalgam is represented in the survey [1], but question about form of existence of the potential-defining of amalgam particles remains controversial to this day. In most studies ammonium amalgam is presented as $\text{NH}_4(\text{Hg})$ [2-6], or $\text{NH}_4(\text{Hg})_n$ [7, 8].

In [9] it has been suggested that the radical NH_4 , obtained by reduction of ammonium cation on a mercury electrode, is dissolved in mercury and gives one electron to the conduction zone.

Based on the linear relationship between the concentration of ammonia in mercury and temperature freezing of amalgam [10] have been concluded that the amalgam ammonium represent a solution of NH_4 radical in mercury. In [11] it has been found that the reduction R_4N^+ cation on mercury, lead and tin are formed solid products:



representing a cation R_4N^+ , associated with a polyanion M_5^- . The stoichiometry of the resulting compounds was proved by elemental analysis.

Based on diamagnetic properties of ammonium amalgam, obtained by reduction of NH_4^+ cation on a mercury electrode at temperatures below point of mercury freezing, it is concluded that the existence of NH_4 radical in mercury is unlikely, therefore amalgam ammonium structure is similar to $[\text{R}_4\text{N}^+(\text{M}_5^-)]_{\text{solid}}$.

According to [11] the name "Ammonium amalgam" does not reflect the nature of the solid compound and "Ammonium - mercury" is more preferred term.

A similar view is expressed in our paper [12]. Unstable free radicals of ammonium and its analogues are stabilized in mercury phase due to the transfer of electron in the zone of mercury conduction. For amalgams of pseudometal hydrides in analogy with amalgams of alkali metals hydrides may be adopted as $\text{R}^+[\text{Hg}_n\text{H}]^-$ structure [13].

Therefore, the aim of this work is the quantum-chemical calculation of the interaction of certain amines with metallic mercury to determine their spatial structure and thermodynamic parameters.

Experimental part. The calculations were performed with use of a standard software package GAUSSIAN'03 [14]. We have used the relativistic potential for a mercury atom, including 46 basic electrons [15]. For light atoms there were used the full-electronic basis set with the inclusion of diffuse and polarization functions 6-311+G(d,p).

Calculations were performed by the hybrid method of density functional B3LYP with the functional Beke B3 [16] and correlation functional Lee, Yang and Parr (LYP) [17]. Currently, this method is generally accepted to describe the thermodynamic characteristics and is best agreed with the experimental values [18]. The geometrical parameters of calculated molecules and ions have been fully optimized, absence of imaginary vibrational frequencies confirmed their stationary character.

The thermodynamic parameters of the molecules calculated were corrected for zero-point vibrational energy (ZPVE) and reduced to normal conditions (298.15K, 1 atm) using thermal corrections to enthalpy and free energy.

The calculations of ammonium cation and NH_4 radical with zero charge, as well as mercury cluster was also carried out in the approximation of natural bond orbitals [19].

On the other hand, these compounds also have been studied by use of ADF program [20]. We used exchange functional OPTX [21], combined with PBE correlation functional [22] with the irreducible Slater triple-zeta + polarization basis set using the frozen-core approximation to the inner electrons. Relativistic effects of heavy atoms have been accounted with use of the regular zero-order approximation (ZORA) [23], which gives more realistic results than the widely used Pauli formalism in the Gaussian package.

Results and their discussion. To assess the "quality" of the calculations it is necessary to rely on some physical and chemical properties of these compounds for which it is known experimental reasonable accurate values. As a last we used the bond lengths, as well as the vibrational frequencies in the IR spectra of some simple mercury compounds.

Fig. 1 shows correlation dependence between experimental [24] and calculated bonds lengths for some mercury compounds:

$$R(\text{exp.}) = -0.14 + 1.03R(\text{calc.}) \quad r = 0.999; s = 0.03; n = 7 \quad (1)$$

In these and the following correlation equations r - is the coefficient of correlation, s - standard deviation, and n - number of compounds included in the correlation.

A similar best dependence was obtained at calculation of the same molecules in the ADF program:

$$R(\text{exp.}) = -0.02 + 1.01R(\text{calc.}) \quad r = 0.999; s = 0.02; n = 7 \quad (2)$$

Table 1 shows the calculated and experimental values of the frequencies of the valence and deformation vibrations in the IR spectra of some mercury compounds [25].

Fig. 2 shows a linear correlation of excellent quality, which testifies that calculations correctly describe the electron-vibrational transitions.

$$\omega(\text{exp.}) = 13.4 + 1.05\omega(\text{calc.}) \quad r = 0.999; s = 12; n = 21 \quad (3)$$

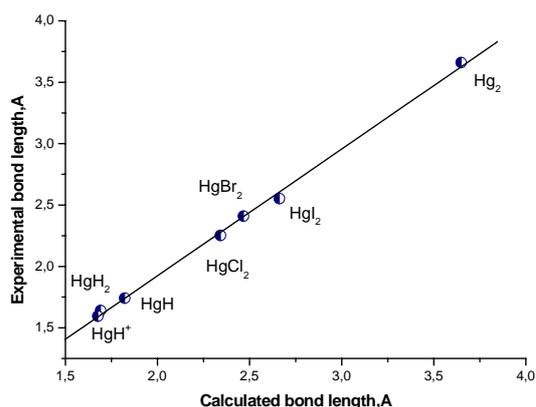


Fig. 1 - Dependence between calculated and experimental lengths of bonds of some simple compounds of mercury.

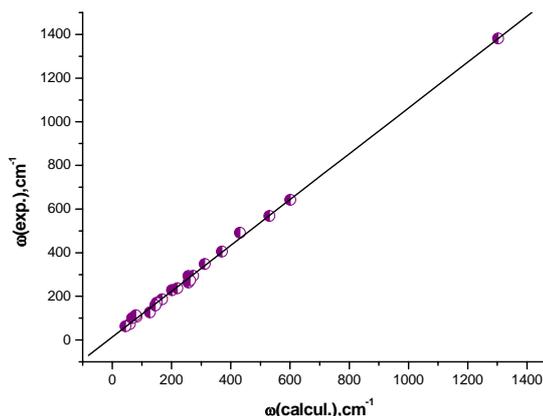


Fig. 2 - Dependence between experimental and calculated frequencies of variations in IR-spectrum of some compounds of mercury.

The good correlation of experimental and calculated lengths of bonds and vibrational frequencies, and the coefficients at $R(\text{calc.})$, close to one, indicates a high reliability of the calculations on the used level of the theory.

Tabl. 1. Experimental and calculated vibrational frequencies in IR spectra of mercury compounds

Compound	$\omega(\text{calc.}) \text{ cm}^{-1}$	$\omega(\text{exp.}) \text{ cm}^{-1}$
HgH	1303	1381
HgF	431	491
HgCl	257	293
HgBr	168	186
HgI	127	126
HgF ₂	150; 531; 601	170; 568; 642
HgCl ₂	82; 312; 370	107; 348; 405
HgBr ₂	59; 202; 273	73; 228; 294
HgI ₂	45; 145; 220	63; 158; 237
HgCl ₃ ⁻	67; 79; 257; 263	100; 113; 263; 273

How it follows from an introduction, principally the interaction of the metallic mercury surface can be implemented both with an ammonium cation, and with a radical of zero charge.

We calculated the two systems, and the results are shown in Table 2. The most significant difference between the ammonium cation and the radical is concluded in a significant reduction in the last index of Wiberg N-H bonds, which represents a decrease of their strength.

In addition, unlike of ammonium cation the lone electron pair of the nitrogen atom is presented in the radical, with a population of about 1 electron. And finally, there is a significant reduction of the energy difference between the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals in the radical.

This allows to confirm that the radical on electron structure is close to the metals in which this

difference is small [25].

We have also carried out similar calculations of several systems NH_4^+Hg_n ($n = 4-6$).

It was found that only systems wherein $n = 4$ are optimized as NH_4^+Hg_4 and NH_4^0Hg_4 in gas phase and increase of number of mercury atoms results in obtainment of a non stable structures with large distances between the cation and mercury atoms.

Tabl 2 – Analysis of natural bond orbitals of ammonium

Molecule	Orbital	Population of orbital, e	Polarization of N-H bond, %	$E_{\text{HOMO}} - E_{\text{LUMO}}$, eV	Index of Wiberg
NH_4^+	Bonding	2.000	73.0	16.1	0.789
NH_4	Bonding	0.946 (α)	62.8 (α)	3.3	0.200 (α)
		0.999 (β)	72.9 (β)		0.197 (β)
	LP (N)	0.967 (α)	100		

For the calculation we used the pseudopotential on mercury atom and the 6-31G (d) basis set for other atoms.

Fig. 3 shows the optimized structure of NH_4^+Hg_4 molecule. It can be seen that its internal part has a strictly tetrahedral structure around of which four mercury atoms are tetrahedral arranged.

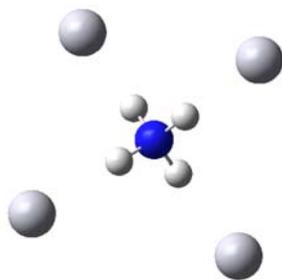


Fig. 3 – Optimized structure of NH_4^+Hg_4 molecule

The distances between the nitrogen and mercury atoms in the compound with the ammonium cation are the same and equal to 3.78\AA (3.82\AA in the ADF program), and the distance in the connection with radical makes up 3.85\AA (4.3\AA in the ADF program). If for ion NH_4^+Hg_4 calculation gives structure with global minimum so at calculation of molecule NH_4^0Hg_4 is observed 3 imaginary frequencies of about 300 cm^{-1} .

These frequencies correspond to the deformation frequencies of NH_4^0 fragment, that indicate on a transition structure in the case of the radical. Some of the molecular orbitals of the NH_4^+Hg_4 cation are shown in Fig. 4.

Calculations show that the 4 higher occupied MO are about the same as for the energy and by type, i.e. the electron density at the same time belongs to all atoms of mercury.

The lower free MO includes all atoms in the molecule, and large electronic density belongs to ammonium ion. Reliable stationary state of NH_4^+Hg_4 cation and transition structure of NH_4^0Hg_4 molecule indicates on greater stability of the first.

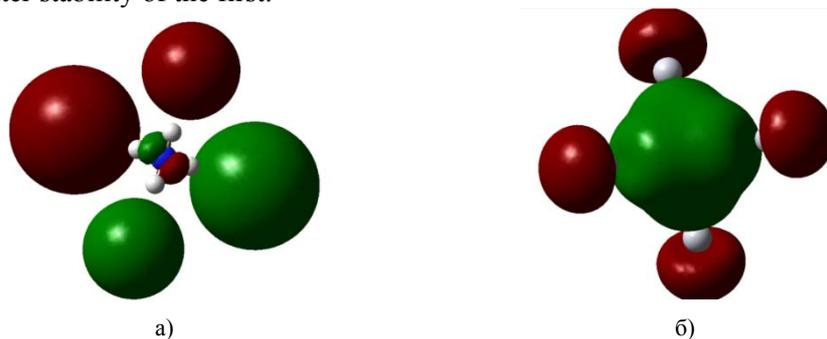


Fig. 4 – Molecular orbitals of molecule NH_4^+Hg_4 : HOMO (a), LUMO (b)

Usage of the method of natural bond orbitals from the point of view of the second-order perturbation theory [19] allows to evaluate the energy interaction between donor and acceptor part of the cluster with account of bonding orbitals and the lone electron pairs of the atoms.

The results of calculation of NH_4^+Hg_4 ion showed that the system becomes stable due to quite significant by the energy of interaction (23 kcal/mol) between lone pairs of electrons of mercury atoms that constitute its s-orbital, with antibonding orbitals of N-H bonds.

Table 3 – Thermodynamic characteristics of $4\text{Hg} + \text{L} = \text{Hg}_4\text{L}$ ($\text{L} = \text{NH}_4^+$, N_2H_4 , NH_2OH) reaction

Molecule	H, a.e.	G, a.e.	ΔH , kcal/mol	ΔG , kcal/mol	E (ADF), kcal/mol	ΔE (ADF), kcal/mol
Hg	-153.080 (-153.154)*	-153.100 (-153.174)*			-4	
NH_4^+	-56.840	-56.860			-377	
NH_4^0	-57.037	-57.06			-474	
NH_4^+Hg_4	-669.200	-669.270	-28	-6	-407	-15
NH_4^0Hg_4	-669.37	-669.43	-6	22	-491	-1
NH_2OH	-131.660	-131.687			-570	
NH_2OHHg_4	-744.000	-744.069	-12	11	-581	5
N_2H_4	-111.696	-111.824			-701	
$\text{N}_2\text{H}_4\text{Hg}_4$	-724.139	-724.209	-77	9	-704	12
NMe_4	-213.982*	-214.018*			-1894	
NMe_4Hg_4	-826.611*	-826.692*	-8	14	-1911	-1

*Values for BP86 functional

For radical NH_4^0Hg_4 the energy of this interaction was significantly lower (10 kcal/mol), which is an additional explanation for the less stability of last structure. Also, both compounds analysis showed no significant population of bond Hg-N, because of the significant distances between the atoms of mercury and an amine.

In addition, the thermodynamic calculations from Table 3 which were conducted by two methods of density functional, lead to the same conclusion.

Not profitable also thermodynamically interaction with the surface of the mercury such amines as hydroxylamine, hydrazine and tetramethylamine, as evidenced the absence of the experimental data for such systems.

This is indicated by positive values of Gibbs free energy and positive or nearly zero change of the total energy of the system in the ADF calculations. In the case of calculation of the tetramethylamine and its compounds with mercury were used BP86 functional, which allows to better optimize the spatially hindered structure.

Conclusions

1. It is shown that the density functional method with use of pseudopotential basis set for mercury atom and 6-311+G(d,p) for other atoms in the software package GAUSSIAN'03 and TZ2P+ program of ADF gives adequate results in predicting of the geometrical parameters and IR spectra of mercury compounds.

2. The analysis of the bonding in the structure of the cation and ammonium radical in the framework of method of the natural bond orbitals was carried out. It is shown that the most likely of interaction with the surface of metallic mercury has an ammonium cation, which is in tetrahedral surrounding with four mercury atoms.

3. The GAUSSIAN'03 and ADF programs calculated the thermodynamic parameters and showed the inability to interact with the surface of metallic mercury such amines as hydroxylamine, hydrazine, and tetra-methylamine.

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ТЫҒЫЗДЫҚ ФУНКЦИОНАЛЫ ТЕОРИЯСЫ НЕГІЗІНДЕ МЕТАЛЛ СЫНАП БЕТІНІҢ АММОНИЙ НЕГІЗДЕРІМЕН ӨЗАРА ӘСЕРІН ТАЛДАУ

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Түйін сөздер: тығыздық функционалының теориясы, жалғанпотенциал, аммоний негіздері, металл сынап, байланыстың табиғи орбитальдары.

Аннотация. Амстердам тығыздық функционалы бағдарламасындағы GAUSSIAN 03 және TZ2P+ бағдарламалық пакетіндегі сынап атомына және басқа атомдарға арналған 6-311+G(d,p) жалған потенциалды базисті жиынын пайдаланып тығыздық функционалы әдісімен газдық фазадағы кейбір сынап құрамдас молекулаларының есептеулері жүргізілді. Аммоний катионы аммоний радикалына салыстырғанда металл сынап бетімен үлкен ықтималдықпен әсерлесетіндігі көрсетілген. Есептелген термиданикалық параметрлер гидроксилламин, гидразин және тетраметиламин сияқты аминдер металл сынап бетімен әсерлесуі мүмкін еместігін көрсетеді.

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