

ISSN 2224-5227

2016 • 1

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ  
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ  
**БАЯНДАМАЛАРЫ**

**ДОКЛАДЫ**

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК  
РЕСПУБЛИКИ КАЗАХСТАН

**REPORTS**

OF THE NATIONAL ACADEMY OF SCIENCES  
OF THE REPUBLIC OF KAZAKHSTAN

ЖУРНАЛ 1944 ЖЫЛДАН ШЫҒА БАСТАҒАН  
ЖУРНАЛ ИЗДАЕТСЯ С 1944 г.  
PUBLISHED SINCE 1944



Бас редактор  
ҚР ҰҒА академигі **М.Ж. Жұрынов**

Редакция алқасы:

хим.ғ. докторы, проф., ҚР ҰҒА академигі **Әдекенов С.М.** (бас редактордың орынбасары), эк.ғ. докторы, проф., ҚР ҰҒА академигі **Әділов Ж.М.**, мед. ғ. докторы, проф., ҚР ҰҒА академигі **Арзықұлов Ж.А.**, техн. ғ. докторы, проф., ҚР ҰҒА академигі **Бишімбаев У.К.**, а.-ш.ғ. докторы, проф., ҚР ҰҒА академигі **Есполов Т.И.**, техн. ғ. докторы, проф., ҚР ҰҒА академигі **Мұтанов Г.М.**, физ.-мат.ғ. докторы, проф., ҚР ҰҒА академигі **Өтелбаев М.О.**, пед. ғ. докторы, проф., ҚР ҰҒА академигі **Пралиев С.Ж.**, геогр.ғ. докторы, проф., ҚР ҰҒА академигі **Северский И.В.**; тарих.ғ. докторы, проф., ҚР ҰҒА академигі **Сыдықов Е.Б.**, физ.-мат.ғ. докторы, проф., ҚР ҰҒА академигі **Тәкібаев Н.Ж.**, физ.-мат.ғ. докторы, проф., ҚР ҰҒА академигі **Харин С.Н.**, тарих ғ. докторы, проф., ҚР ҰҒА корр. мүшесі **Әбүсейітова М.Х.**, экон. ғ. докторы, проф., ҰҒА корр. мүшесі **Бейсембетов И.К.**, биол. ғ. докторы, проф., ҚР ҰҒА корр. мүшесі **Жамбакин К.Ж.**, тарих ғ. докторы, проф., ҚР ҰҒА корр. мүшесі **Кәрібаев Б.Б.**, мед. ғ. докторы, проф., ҚР ҰҒА корр. мүшесі **Локшин В.Н.**, геол.-мин. ғ. докторы, проф., ҚР ҰҒА корр. мүшесі **Өмірсеріков М.Ш.**, физ.-мат. ғ. докторы, проф., ҚР ҰҒА корр. мүшесі **Рамазанов Т.С.**, физ.-мат. ғ. докторы, проф., ҚР ҰҒА корр. мүшесі **Садыбеков М.А.**, хим.ғ. докторы, проф., ҚР ҰҒА корр. мүшесі **Сатаев М.И.**; ҚР ҰҒА құрметті мүшесі, а.-ш.ғ. докторы, проф. **Омбаев А.М.**

Редакция кеңесі:

Украинаның ҰҒА академигі **Гончарук В.В.** (Украина), Украинаның ҰҒА академигі **Неклюдов И.М.** (Украина), Беларусь Республикасының ҰҒА академигі **Гордиенко А.И.** (Беларусь), Молдова Республикасының ҰҒА академигі **Дука Г.** (Молдова), Тәжікстан Республикасының ҰҒА академигі **Илолов М.И.** (Тәжікстан), Қырғыз Республикасының ҰҒА академигі **Эркебаев А.Э.** (Қырғызстан), Ресей ҒА корр. мүшесі **Величкин В.И.** (Ресей Федерациясы); хим.ғ. докторы, профессор **Марек Сикорски** (Польша), тех.ғ. докторы, профессор **Потапов В.А.** (Украина), биол.ғ. докторы, профессор **Харун Парлар** (Германия), профессор **Гао Энджун** (КХР), филос. ғ. докторы, профессор **Стефано Перни** (Ұлыбритания), ғ. докторы, профессор **Богуслава Леска** (Польша), философия ғ. докторы, профессор **Полина Прокопович** (Ұлыбритания), профессор **Вуйцик Вольдемар** (Польша), профессор **Нур Изура Удзир** (Малайзия), д.х.н., профессор **Нараев В.Н.** (Ресей Федерациясы)

Главный редактор  
академик НАН РК **М.Ж. Журинов**

Редакционная коллегия:

доктор хим. наук, проф., академик НАН РК **С.М. Адекенов** (заместитель главного редактора), доктор экон. наук, проф., академик НАН РК **Ж.М. Адилов**, доктор мед. наук, проф., академик НАН РК **Ж.А. Арзыкулов**, доктор техн. наук, проф., академик НАН РК **В.К. Бишимбаев**, доктор сельскохозяйств. наук, проф., академик НАН РК **Т.И. Есполов**, доктор техн. наук, проф., академик НАН РК **Г.М. Мутанов**, доктор физ.-мат. наук, проф., академик НАН РК **М.О. Отелбаев**, доктор пед. наук, проф., академик НАН РК **С.Ж. Пралиев**, доктор геогр. наук, проф., академик НАН РК **И.В. Северский**; доктор ист. наук, проф., академик НАН РК **Е.Б. Сыдыков**, доктор физ.-мат. наук, проф., академик НАН РК **Н.Ж. Такибаев**, доктор физ.-мат. наук, проф., академик НАН РК **С.Н. Харин**, доктор ист. наук, проф., чл.-корр. НАН РК **М.Х. Абусейтова**, доктор экон. наук, проф., чл.-корр. НАН РК **И.К. Бейсембетов**, доктор биол. наук, проф., чл.-корр. НАН РК **К.Ж. Жамбакин**, доктор ист. наук, проф., чл.-корр. НАН РК **Б.Б. Карибаев**, доктор мед. наук, проф., чл.-корр. НАН РК **В.Н. Локшин**, доктор геол.-мин. наук, проф., чл.-корр. НАН РК **М.Ш. Омирсериков**, доктор физ.-мат. наук, проф., чл.-корр. НАН РК **Т.С. Рамазанов**, доктор физ.-мат. наук, проф., чл.-корр. НАН РК **М.А. Садыбеков**, доктор хим. наук, проф., чл.-корр. НАН РК **М.И. Сатаев**; почетный член НАН РК, доктор сельскохозяйств. наук, проф., **А.М. Омбаев**

Редакционный совет:

академик НАН Украины **Гончарук В.В.** (Украина), академик НАН Украины **И.М. Неклюдов** (Украина), академик НАН Республики Беларусь **А.И.Гордиенко** (Беларусь), академик НАН Республики Молдова **Г. Дука** (Молдова), академик НАН Республики Таджикистан **М.И. Илолов** (Таджикистан), член-корреспондент РАН **Величкин В.И.** (Россия); академик НАН Кыргызской Республики **А.Э. Эркебаев** (Кыргызстан), д.х.н., профессор **Марек Сикорски** (Польша), д.т.н., профессор **В.А. Потапов** (Украина), д.б.н., профессор **Харун Парлар** (Германия), профессор **Гао Энджун** (КНР), доктор философии, профессор **Стефано Перни** (Великобритания), доктор наук, профессор **Богуслава Леска** (Польша), доктор философии, профессор **Полина Прокопович** (Великобритания), профессор **Вуйцик Вольдемар** (Польша), профессор **Нур Изура Удзир** (Малайзия), д.х.н., профессор **В.Н. Нараев** (Россия)

«Доклады Национальной академии наук Республики Казахстан» ISSN 2224-5227

Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан» (г. Алматы)

Свидетельство о постановке на учет периодического печатного издания в Комитете информации и архивов Министерства культуры и информации Республики Казахстан №5540-Ж, выданное 01.06.2006 г.

Периодичность: 6 раз в год. Тираж: 2000 экземпляров

Адрес редакции: 050010, г.Алматы, ул.Шевченко, 28, ком.218-220, тел. 272-13-19, 272-13-18

<http://nauka-nanrk.kz>, [reports-science.kz](http://reports-science.kz)

Адрес типографии: ИП «Аруна», г.Алматы, ул.Муратбаева, 75

©Национальная академия наук Республики Казахстан, 2016 г.

E d i t o r i n c h i e f

**M.Zh. Zhurinov**, academician of NAS RK

Editorial board:

**S.M. Adekenov** (deputy editor in chief), Doctor of Chemistry, prof., academician of NAS RK; **Zh.M. Adilov**, Doctor of Economics, prof., academician of NAS RK; **Zh.A. Arzykulov**, Doctor of Medicine, prof., academician of NAS RK; **V.K. Bishimbayev**, Doctor of Engineering, prof., academician of NAS RK; **T.I. Yespolov**, Doctor of Agriculture, prof., academician of NAS RK; **G.M. Mutanov**, Doctor of Physics and Mathematics, prof., academician of NAS RK; **M.O. Otelbayev**, Doctor of Physics and Mathematics, prof., academician of NAS RK; **S.Zh. Praliyev**, Doctor of Education, prof., academician of NAS RK; **I.V. Seversky**, Doctor of Geography, prof., academician of NAS RK; **Ye.B. Sydykov**, Doctor of Historical Sciences, prof., academician of NAS RK; **N.Zh. Takibayev**, Doctor of Physics and Mathematics, prof., academician of NAS RK; **S.N. Kharin**, Doctor of Physics and Mathematics, prof., academician of NAS RK; **M.Kh. Abuseitova**, Doctor of Historical Sciences, prof., corr. member of NAS RK; **I.K. Beisembetov**, Doctor of Economics, prof., corr. member of NAS RK; **K.Zh. Zhambakin**, Doctor of Biological Sciences, prof., corr. member of NAS RK; **B.B. Karibayev**, Doctor of Historical Sciences, prof., corr. member of NAS RK; **V.N. Lokshin**, Doctor of Medicine, prof., corr. member of NAS RK; **M.Sh. Omirserikov**, Doctor of Geology and Mineralogy, prof., corr. member of NAS RK; **T.S. Ramazanov**, Doctor of Physics and Mathematics, prof., corr. member of NAS RK; **M.A. Sadybekov**, Doctor of Physics and Mathematics, prof., corr. member of NAS RK; **M.I. Satayev**, Doctor of Chemistry, prof., corr. member of NAS RK; **A.M. Ombayev**, Honorary Member of NAS RK, Doctor of Agriculture, prof.

Editorial staff:

**V.V. Goncharuk**, NAS Ukraine academician (Ukraine); **I.M. Neklyudov**, NAS Ukraine academician (Ukraine); **A.I. Gordienko**, NAS RB academician (Belarus); **G. Duca**, NAS Moldova academician (Moldova); **M.I. Iolov**, NAS Tajikistan academician (Tajikistan); **A.E. Erkebayev**, NAS Kyrgyzstan academician (Kyrgyzstan); **V.I. Velichkin**, RAS corr.member (Russia); **Marek Sikorski**, Doctor of Chemistry, prof. (Poland); **V.A. Potapov**, Doctor of Engineering, prof. (Ukraine); **Harun Parlar**, Doctor of Biological Sciences, prof. (Germany); **Gao Endzhun**, prof. (PRC); **Stefano Perni**, Doctor of Philosophy, prof. (UK); **Boguslava Leska**, dr, prof. (Poland); **Pauline Prokopovich**, Doctor of Philosophy, prof. (UK); **Wójcik Waldemar**, prof. (Poland), **Nur Izura Udzir**, prof. (Malaysia), **V.N. Narayev**, Doctor of Chemistry, prof. (Russia)

**Reports of the National Academy of Sciences of the Republic of Kazakhstan.**

ISSN 2224-5227

Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty)

The certificate of registration of a periodic printed publication in the Committee of Information and Archives of the Ministry of Culture and Information of the Republic of Kazakhstan N 5540-Ж, issued 01.06.2006

Periodicity: 6 times a year

Circulation: 2000 copies

Editorial address: 28, Shevchenko str., of.219-220, Almaty, 050010, tel. 272-13-19, 272-13-18,

<http://nauka-nanrk.kz/> [reports-science.kz](http://reports-science.kz)

Address of printing house: ST "Aruna", 75, Muratbayev str, Almaty

© National Academy of Sciences of the Republic of Kazakhstan, 2016

REPORTS OF THE NATIONAL ACADEMY OF SCIENCES  
OF THE REPUBLIC OF KAZAKHSTAN

ISSN 2224-5227

Volume 1, Number 305 (2016), 9 – 14

UDK 541.1+530.145

ESTIMATIONS OF THE ISOMER MÖSSBAUER SHIFTS FOR  
TETRAOXOFERRATES USING ADF PACKAGE

O. Kh. Poleshchuk<sup>1</sup>, S.K. Dedushenko<sup>2</sup>, M.N. Ermakhanov<sup>3</sup>,  
P.A. Saidakhmetov<sup>4</sup>, M.A. Nurullaev<sup>5</sup>

<sup>1</sup>National Research Tomsk Polytechnic University, Tomsk, Russia

<sup>2</sup>Department of Chemistry, Moscow State University, Moscow, Russia

<sup>3</sup>M.Auezov South Kazakhstan State University, Shymkent, RK

[poleshch@tspu.edu.ru](mailto:poleshch@tspu.edu.ru), [myrza1964@mail.ru](mailto:myrza1964@mail.ru), [timpf\\_ukgu@mail.ru](mailto:timpf_ukgu@mail.ru), [nurmarat75@mail.ru](mailto:nurmarat75@mail.ru)

**Key words:** Density Functional Theory, ADF, Mössbauer spectroscopy, ferrates

**Abstract.** <sup>7</sup>Fe isomer shifts and the electron density on iron nucleus for a range of tetraoxoferrate ions have been analyzed by means of DFT calculations. The bond lengths and the electron density on the nuclei obtained by our calculations substantially corresponded to the known structural and Mössbauer data. For ferrates the isomer shift depends on the 4s-orbital population. The results obtained allowed us to estimate the isomer shifts for tetraoxoferrate(VII), KFeO<sub>4</sub>, and iron(VIII) oxide, FeO<sub>4</sub>.

### 1. Introduction

There is constantly growing interest in iron in high oxidation states primarily due to its high potential in water treatment [1, 2]. Ferrates of alkali metals contain complex tetraoxoferrate anions [FeO<sub>4</sub>]<sup>n-</sup> (n=4÷2), which give ferrate(VI)-anion, FeO<sub>4</sub><sup>2-</sup>, when come into water. FeO<sub>4</sub><sup>2-</sup>-ion is a very powerful oxidant. They are able to neutralize extremely toxic substances, whereas common oxidizing agents used in water treatment, such as chlorine and ozone, often result in more toxic products. Ferrates (VII) and (VIII) are exotic part of modern inorganic chemistry. But these compounds could be much stronger oxidizers than ferrate (VI). That is why it is very important to know their Mössbauer parameters. This could allow us to detect iron (VII) and (VIII) in the reaction mixture betimes and to optimize the synthetic way.

### 2. Calculations

To calculate the geometrical parameters of the isolated ions [Fe<sup>m</sup>O<sub>4</sub>]<sup>m-8</sup> (m>3) obtained with using Amsterdam Density Functional. Geometry optimisation for ions calculated with using exchange functional OPTX [3] conjunction with PBE correlation functional [4] and all-electron TZP basis set of Slater's o-orbitals, using approximation of frozen core in attitude to core electrons. A scalar relativistic effect was considered with using regular approximation of zero-order ZORA [5]. The applying of this basis set is better with respect to accuracy and efficiency. The analysis of the atomic charge and populations of atomic orbitals has been done using the NBO [6] approximation within the GAUSSIAN'03 [7] program.

Isomer shifts in this paper are related to  $\alpha$ -iron and are presented in [mm·s<sup>-1</sup>].

### 3. Results and discussion

First, the geometries of ions [FeO<sub>4</sub>]<sup>n-</sup> (n=0÷4) were optimized by the above mentioned procedure. The calculated Fe-O bond lengths are presented in Table 1. To check the accuracy of our quantum-chemical calculations it is necessary to compare the experimental and calculated geometries of molecules. For the comparison we used the structural data for the following known ferrates: Na<sub>4</sub>FeO<sub>4</sub> [8], K<sub>3</sub>FeO<sub>4</sub> [9], K<sub>2</sub>FeO<sub>4</sub> [10, 11]. In these compounds iron is in practically regular tetrahedral oxygen arrangement. The average Fe-O distances used for comparison are presented in Figure 1.

The correlation diagram is presented in Figure 1 and gives us very good results:

$$R_{\text{Fe-O}}^{\text{exp.}} [\text{Å}] = -0.5 + 1.3 R_{\text{Fe-O}}^{\text{cal.}} [\text{Å}] \quad (r=0.999; s=0.004; n=3)$$

Obtained earlier [15] by B3LYP/DGDZVP method with using Gaussian 03 program such correlation

was approximately the same quality

$$R_{\text{Fe-O}}^{\text{exp.}} [\text{\AA}] = -0.2 + 1.1 R_{\text{Fe-O}}^{\text{cal.}} [\text{\AA}] \quad (r=0.987; s=0.02; n=3)$$

In this and subsequent correlation equations  $r$  is a correlation coefficient,  $s$  is the standard curve fit error, and  $n$  is the number of compounds.

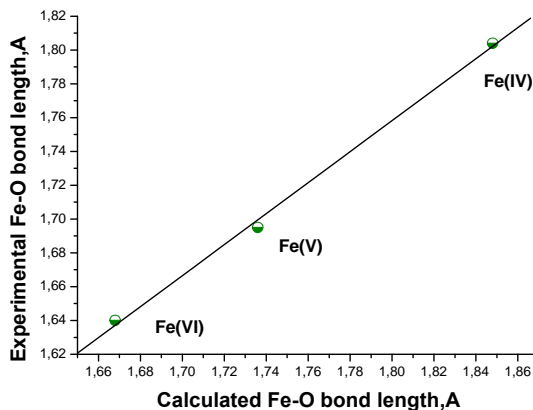


Figure 1. Dependence between experimental and calculated by BP86/TZ2P+ method Fe-O bond length

Basically, for obtaining of dependences between formal degrees of oxidation of the iron ions it is possible to use various schemes of the calculation of different effective charge on atoms. In this paper we used the analysis of an effective charge by Voronoi scheme [16] which is considered one of optimal for estimation atomic charges.

The calculations showed that the increasing of the iron oxidation state (OS) lead to decreasing both natural charge on the oxygen atom ( $Q_{\text{O}}$ ) and natural charge of the iron atom ( $Q_{\text{Fe}}$ ). The respective dependencies are described by the following correlation equations:

$$Q_{\text{O}} [e] = -2.0 + 0.24\text{OS} \quad (r = 0.9999; s = 0.007; n = 7)$$

$$Q_{\text{Fe}} [e] = 0.1 + 0.03\text{OS} \quad (r = 0.982; s = 0.01; n = 7)$$

Increasing of the oxidation state is also accompanied by the increase of the electron density on the iron nucleus ( $\rho_{\text{O}}$ ) (Figure 2.)

$$\rho_{\text{O}} [a_0^{-3}] = 14824 + 1.06\text{OS} \quad (r = 0.982; s = 0.5; n = 7)$$

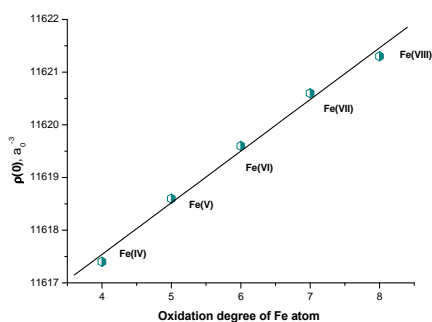


Figure 2. Dependence between electron density on Fe nuclei (calculated by BP86/TZ2P+ method) and ions oxidations state

**Table 1.** Optimized by BP86/TZ2P+ method and experimental parameters for tetraoxoferrates (IV) – (VIII)

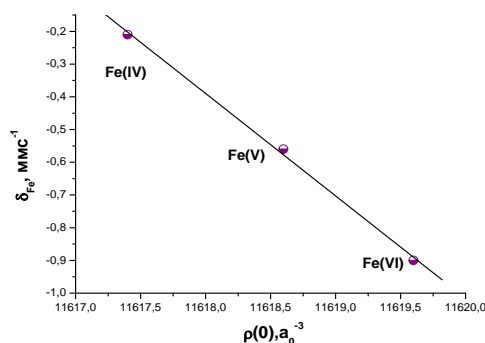
Oxidation state of iron	$R_{\text{Fe-O}}^{\text{cal.}}$ , Å	$R_{\text{Fe-O}}^{\text{exp.}}$ , Å	$\delta_{\alpha\text{-Fe}}^{\text{cal.}}$ , mm·s <sup>-1</sup>	$\delta_{\alpha\text{-Fe}}^{\text{exp.}}$ , mm·s <sup>-1</sup>	$\rho_0 \cdot a_0^{-3}$	$N_s, e$
+4	1.848	1.804 for Na <sub>4</sub> FeO <sub>4</sub>	-0.18	-0.22 for Na <sub>4</sub> FeO <sub>4</sub>	14827.0	0.223
+5	1.736	1.695 for K <sub>3</sub> FeO <sub>4</sub>	-0.55	-0.55 for K <sub>3</sub> FeO <sub>4</sub>	14828.7	0.241
+6	1.668	1.640 for K <sub>2</sub> FeO <sub>4</sub>	-0.87	-0.90 for K <sub>2</sub> FeO <sub>4</sub>	14830.1	0.255
+7	1.619	-	-1.18	-	14831.3	0.268
+8	1.586	-	-1.40	-	14832.3	0.277

The similar correlation presented earlier [15] had a few more correlation parameter, but ions Fe(II) and Fe (III) are excluded from correlation dependence calculated by B3LYP/dgdzvp

$$\rho_0 [a_0^{-3}] = 11613.6 + 0.98 \text{ OS} \quad (r = 0.996; s = 0.16; n = 5)$$

Finally  $\rho_0$  has been compared with experimental isomer shifts of well-known ferrates (Figure 3). This dependency has also good correlation parameters:

$$\delta [\text{mm} \cdot \text{s}^{-1}] = 2997 - 0.20215 \rho_0 [a_0^{-3}] \quad (r = 0.980; s = 0.07; n = 3)$$



**Figure 3.** Dependence between experimental shift and calculated relativistic electronic densities at the <sup>57</sup>Fe nucleus (by BP86/TZ2P+ method)

The correlation dependences obtained by both methods have allowed to use calculated electronic density on Fe nucleus to estimate of isomer shifts for tetraoxoferrate (VII) and (VIII) (-1.18 and -1.40 mm·s<sup>-1</sup> from B3LYP/dgdzvp method [15], as well as -1.15 and -1.35 mm·s<sup>-1</sup> from BP86/TZ2P+ method, in this paper, relative to  $\alpha$ -Fe respectively). Obviously, using of different methods of calculation has allowed obtaining almost identical isomer shifts which indicates a sufficiently precision of these calculations and their proximity to the experimental values.

It will be noted that absorption lines in the respective range were already observed formerly at the spectra of Na<sub>4</sub>FeO<sub>4</sub> [12]. This compound decomposes at room temperature by disproportionation mechanism. During this multistage process several higher oxidation states of iron can be observed. Interaction of Na<sub>4</sub>FeO<sub>4</sub> with Na<sub>2</sub>O<sub>2</sub> also allowed us to synthesized iron derivatives showing absorption lines with extremely low shifts [12]. The line with isomer shift -1.52 mm·s<sup>-1</sup> (at 78 K) was also observed in the frozen solutions, obtained by anodic dissolution of metallic iron in concentrated NaOH (14M NaOH) at high current densities [17]. This line was assigned to Fe(VIII).

It is well known that for Mössbauer atoms the magnitude of the isomer shift depends simultaneously on the s-, p- and d-orbital populations of these atoms [18]. Earlier for various so-called Mössbauer atoms

very good correlations between isomer shifts and orbital populations calculated at B3LYP/3-21G(d) by similar procedure have been found [19-22]. For iodine compounds the main contribution to isomer shift comes from the 5s-orbital population, but for tin and antimony compounds a considerable contribution comes from the shielding by 5p-orbitals. For the Au(I) and Au(III) compounds the dependences between the isomer shift and the orbital populations include the direct effect of the valence-shell s-electrons and their shielding of the d-electrons. According to these results it was possible to confirm the conclusion about the greater contribution of the 6s-orbital than 5d-orbital of a gold atom to the isomer shift. If in Au(I) compounds the chemical bonding is determined basically by s- and to a lower extent by d-orbitals of the central atom, in Au(III) compounds the contribution of d-orbital is considerably increased, that is coordinated by a natural image with the increase of the number gold atom bonds. The similar results were obtained by us at B3LYP/LanL2DZ level of Pt(II) and Pt(IV) compounds [20]. For Pt(II) compounds the main contribution to isomer shift comes from the 6s-orbital population, but for Pt(IV) compounds the shielding of the nucleus by 5d-orbitals brings in the greater contribution.

The main observed trends in the variations of the isomer shifts for ferrates can now be interpreted in terms of the valence electronic populations, which depend on iron oxidation state. Our calculation leads to the conclusion that in tetraoxoferrate ions the main contribution to isomer shift brings the 4s-electrons, which is confirmed by the excellent correlation equation:

$$\delta[\text{mm}\cdot\text{s}^{-1}] = -0.214 - 0.045N_s [e] \quad (r=0.999; s=0.001; n=5)$$

This correlation is valid for both calculated and experimental isomer shifts of ferrates (IV)-(VIII).

An addition of the  $N_d$  population increment to the last equation impairs the quality of the correlation; the standard curve fit error being 0.01 mm·s<sup>-1</sup>. Thus, our calculations show that the shielding of the iron nucleus by d-electrons does not influence on the isomer shift.

УДК541.1+530.145

Оценка изомерных мессбауэровских сдвигов для тетраоксоферратов с помощью ADF пакета

О. Х. Поleshch<sup>1</sup>, С.К. Дедушенко<sup>2</sup>, М.Н. Ермаханов<sup>3</sup>,  
П.А. Саидахметов<sup>4</sup>, М.А. Нуруллаев<sup>5</sup>

<sup>1</sup>Национальный исследовательский Томский политехнический университет, Томск, Россия

<sup>2</sup>Московский государственный университет, Москва, Россия

<sup>3</sup>Южно-Казахстанский государственный университет им. М. Ауезова, Шымкент, РК  
[polshch@tspu.edu.ru](mailto:polshch@tspu.edu.ru), [myrza1964@mail.ru](mailto:myrza1964@mail.ru), [timpf\\_ukgu@mail.ru](mailto:timpf_ukgu@mail.ru), [nurmarat75@mail.ru](mailto:nurmarat75@mail.ru)

**Ключевые слова:** теория функционала плотности, ADF (Амстердамский функционал плотности), мессбауэровская спектроскопия, ферраты

**Аннотация.** С помощью расчетов DFT (теория функционала плотности) были проанализированы изомерные сдвиги <sup>57</sup>Fe и электронная плотность на ядрах железа для ионов тетраоксоферратов. Полученные по нашим расчетам длины связей и плотность электронов на ядрах хорошо согласуются с известными структурными и мессбауэровскими данными. Для ферратов изомерные сдвиги зависят от заселенности 4s-орбитали. Полученные результаты позволили оценить изомерные сдвиги для тетраоксоферратов (VII), KFeO<sub>4</sub> и оксида железа (VIII), FeO<sub>4</sub>.

## REFERENCES

[1] Sharma V.K., Jiang Q. and Bouzek K. Innovative Ferrate (VI) Technology in Water and Wastewater Treatment. *Prague: ICT Press*, 2004, P. 9-19 (in Eng.).

[2] *Ferrates: Properties and Applications in Water and Wastewater Treatment: Preprints of Extended Abstracts, Division of Environmental Chemistry of the American Chemical Society* 46-2540, 2006 (in Eng.).

[3] Handy N.C., Cohen A.J. *Mol. Phys.*, 2001, vol. 99, P.403 – 412 (in Eng.).

[4] Perdew J.P., Burke K., Ernzerhof M. *Phys. Rev. Lett.*, 1996, vol.77, P.3865– 3868 (in Eng.).

[5] Velde G., Bickelhaupt F.M., Gisbergenvan S.J.A., et al. *J. Comput. Chem.*, 2001, vol.22, no.9, P.931 – 967 (in Eng.).

[6] Reed A.E., Curtiss L.A., Weinhold F. *Chem. Rev.*, 1988, vol.88, no.6, P.899 – 926 (in Eng.).

[7] Gaussian 03, Revision B.03, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi V. Barone, B. Mennucci, M. Cossi, G.



Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz I. Komaromi, R.L. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J.A. Pople. *Gaussian, Inc., Pittsburgh PA, 2003*(in Eng.).

- [8] Jeannot C., Malaman B., Gerardin R. and Oulladiat B. *J. Solid State Synth.*, **2002**, vol.165, P.266 – 277 (in Eng.).  
 [9] Hoppe R., Mader K.Z. *Anorg. Allg. Chem.*, **1990**, vol.586, P.115 (in Eng.).  
 [10] Audette R.J., Quall J.W., Black W.H., Robertson B.E. *J. Solid State Chem.*, **1973**, vol.8, P.43 – 49 (in Eng.).  
 [11] Hope M.L., Schlemper E.O., Murmann R.K. *Acta Cryst.*, **1982**, vol. B38, P.2237 – 2239 (in Eng.).  
 [12] Dedushenko S.K., Kholodkovskaya L.N., Perfiliev Yu.D., Kiselev Y.M., Saprykin A.A., Kamozin P.N., Lemesheva D.G. *J. Alloys Compd.*, **1997**, vol.262-263, P.78–80 (in Eng.).  
 [13] Dedushenko S.K., Perfiliev Yu.D., Saprykin A.A. *Hyperfine Interactions*, **2008**, vol.185, P.197– 202 (in Eng.).  
 [14] Dedushenko S.K., Perfiliev Yu.D., Goldfeld M.G., Tsapin A.I. *Hyperfine Interactions*, **2001**, vol.136, N3, P.373– 377 (in Eng.).  
 [15] Poleshchuk O., Kruchkova N., Perfiliev Yu., Dedushenko S. *Journal of Physics: Conference Series*, **2010**, vol.217, issue number, article ID012041, (in Eng.) (<http://dx.doi.org/10.1088/1742-6596/217/1/012041>).  
 [16] Guerra C.F., Bichelaupt F.M., Snijders J.G., Baerends E.J. *Chem.-A Eur. J.*, **1999**, vol.5, P.3581 – 3594 (in Eng.).  
 [17] Kopelev N.S., Perfiliev Yu.D., Kiselev Yu. M. *J. Radioanal. Nucl. Chem.*, **1992**, vol.162, P.239 – 251 (in Eng.).  
 [18] Parish R.V. *Coord. Chem. Rev.* **1982**, vol.42, P.1 (in Eng.).  
 [19] Poleshchuk O.Kh., Latosinska J.N., Yakimov V.G. *Chem. Phys.*, **2000**, vol.2, P.1877 – 1882 (in Eng.).  
 [20] Poleshchuk O.Kh., Shevchenko E.L., Branchadell V., Schulz A. *Hyperfine Interactions*, **2004**, vol.159, P.293 (in Eng.).  
 [21] Poleshchuk O.Kh., Branchadell V., Ritter R.A., Fateev A.V. *Hyperfine Interactions*, **2008**, vol.181, P.27 (in Eng.).  
 [22] Poleshchuk O.Kh., Fateev A.V., Legon A.C., Frenking G. *Trends in Physical Chemistry*, **2014**, vol. 15, P. 13 (in Eng.).

#### ADF пакетінің көмегімен тетраоксоферраттар үшін изомерлік Мессбауэрлік ығысуларды бағалау

О. Х. Поleshchuk<sup>1</sup>, С.К. Дедушенко<sup>2</sup>, М.Н. Ермаханов<sup>3</sup>, П.А. Саидрахметов<sup>4</sup>,  
М.А. Нуруллаев<sup>5</sup>

<sup>1</sup>Томск ұлттық зерттеу политехникалық университеті, Томск, Ресей

<sup>2</sup>Химия кафедрасы, Мәскеу мемлекеттік университеті, Мәскеу, Ресей

<sup>3</sup>М.Әуезов атындағы Оңтүстік Қазақстан мемлекеттік университеті, Шымкент қ.,  
Қазақстан Республикасы

[poleshch@tspu.edu.ru](mailto:poleshch@tspu.edu.ru), [myrza1964@mail.ru](mailto:myrza1964@mail.ru), [timpf\\_ukgu@mail.ru](mailto:timpf_ukgu@mail.ru), [nurmarat75@mail.ru](mailto:nurmarat75@mail.ru)

**Түйін сөздер:** тығыздық функционалының теориясы, ADF (тығыздықтың Амстердам функционалы), мессбауэр спектроскопиясы, ферраттар.

**Аннотация.** DFT(тығыздық функционалы теориясы) есептеулер көмегімен <sup>57</sup>Fe изомерлік ығысулары және тетраоксоферраттар иондары үшін темір ядросындағы электрондық тығыздықтары талданды. Біздің есептеулер бойынша алынған байланыс ұзындығы мен ядролардағы электрондардың тығыздықтары белгілі құрылымдық және мессбауэр мәліметтермен жақсы сәйкес келеді. Ферраттар үшін изомерлік ығысулар 4s-орбиталінің тығыздығына тәуелді болады. Алынған нәтижелер тетраоксоферраттар (VII), KFeO<sub>4</sub> және темір оксидінің (VIII), FeO<sub>4</sub> изомерлік ығысуларын есептеуге мүмкіндік берді.

**Олег Хемович Поleshchuk**

х.ғ.д.,  
Томск ұлттық зерттеу  
политехникалық  
университеті,  
Ресей

**С.К. Дедушенко**

х.ғ.д.,  
Химия кафедрасы, Мәскеу  
мемлекеттік университеті,  
Мәскеу, Ресей

**Ермаханов Мырзабек  
Нысанбекулы**

х.ғ.к.,  
М.Әуезов атындағы

**Олег Хемович Поleshchuk**

д.х.н.,  
Национальный  
исследовательский Томский  
политехнический  
университет,  
Томск, Россия

**С.К. Дедушенко**

д. х. н., кафедра Химии  
Московский государственный  
университет,  
Москва, Россия

**Ермаханов Мырзабек  
Нысанбекулы**

к.х.н.,  
Южно-Казахстанский

**Oleg Khemovich Poleshchuk**

D.Sc.,  
National Research Tomsk  
Polytechnic University,  
Tomsk, Russia

**S.K. Dedushenko**

D.Sc.,  
Department of Chemistry,  
Moscow State University,  
Moscow, Russia

**Myrzabek Nysanbekuly Erm  
akhanov**

c.ch. s., M. Auezov South  
Kazakhstan state University,

[poleshch@tspu.edu.ru](mailto:poleshch@tspu.edu.ru)

[myrza1964@mail.ru](mailto:myrza1964@mail.ru)

Оңтүстік Қазақстан мемлекеттік университеті Шымкент қ., Қазақстан Республикасы	государственный университет имени М.Ауезова, Шымкент, РК	Shymkent, RK	
<b>Пулат Аблатыевич Саидахметов</b> ф.-м.ғ.к., М.Әуезов атындағы Оңтүстік Қазақстан мемлекеттік университеті Шымкент қ., Қазақстан Республикасы	<b>Пулат Аблатыевич Саидахметов</b> к.ф.-м.н., зав.кафедрой, Южно-Казахстанский государственный университет имени М.Ауезова, Шымкент, РК	<b>Pulat Ablatyevich Saidakhmetov</b> с.п.-м. с., Head of Department, M.Auezov South Kazakhstan state University, Shymkent, RK	<a href="mailto:timpf_ukgu@mail.ru">timpf_ukgu@mail.ru</a>
<b>Нуруллаев Марат Амангельдыевич</b> оқытушы, М.Әуезов атындағы Оңтүстік Қазақстан мемлекеттік университеті, Шымкент қ., Қазақстан Республикасы	<b>Нуруллаев Марат Амангельдыевич</b> преподаватель, Южно-Казахстанский государственный университет имени М.Ауезова, Шымкент, РК	<b>Nurullaev Marat Amangeldyevich</b> teacher M.Auezov South Kazakhstan state University, Shymkent, RK	<a href="mailto:nurmarat75@mail.ru">nurmarat75@mail.ru</a>

**PUBLICATION ETHICS AND PUBLICATION MALPRACTICE  
IN THE JOURNALS OF THE NATIONAL ACADEMY OF SCIENCES  
OF THE REPUBLIC OF KAZAKHSTAN**

For information on Ethics in publishing and Ethical guidelines for journal publication see <http://www.elsevier.com/publishingethics> and <http://www.elsevier.com/journal-authors/ethics>.

Submission of an article to the National Academy of Sciences of the Republic of Kazakhstan implies that the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis or as an electronic preprint, see <http://www.elsevier.com/postingpolicy>), that it is not under consideration for publication elsewhere, that its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder. In particular, translations into English of papers already published in another language are not accepted.

No other forms of scientific misconduct are allowed, such as plagiarism, falsification, fraudulent data, incorrect interpretation of other works, incorrect citations, etc. The National Academy of Sciences of the Republic of Kazakhstan follows the Code of Conduct of the Committee on Publication Ethics (COPE), and follows the COPE Flowcharts for Resolving Cases of Suspected Misconduct ([http://publicationethics.org/files/u2/New\\_Code.pdf](http://publicationethics.org/files/u2/New_Code.pdf)). To verify originality, your article may be checked by the originality detection service Cross Check <http://www.elsevier.com/editors/plagdetect>.

The authors are obliged to participate in peer review process and be ready to provide corrections, clarifications, retractions and apologies when needed. All authors of a paper should have significantly contributed to the research.

The reviewers should provide objective judgments and should point out relevant published works which are not yet cited. Reviewed articles should be treated confidentially. The reviewers will be chosen in such a way that there is no conflict of interests with respect to the research, the authors and/or the research funders.

The editors have complete responsibility and authority to reject or accept a paper, and they will only accept a paper when reasonably certain. They will preserve anonymity of reviewers and promote publication of corrections, clarifications, retractions and apologies when needed. The acceptance of a paper automatically implies the copyright transfer to the National Academy of sciences of the Republic of Kazakhstan.

The Editorial Board of the National Academy of sciences of the Republic of Kazakhstan will monitor and safeguard publishing ethics.

Правила оформления статьи для публикации в журнале смотреть на сайте:

[www:nauka-nanrk.kz](http://www.nauka-nanrk.kz)

<http://www.reports-science.kz/index.php/ru/>

Редакторы *М. С. Ахметова, Д. С. Аленов, Т.А. Апендиев*  
Верстка на компьютере *С.К. Досаевой*

Подписано в печать 05.02.2016.

Формат 60x881/8. Бумага офсетная. Печать – ризограф.  
10,25 п.л. Тираж 2000. Заказ 1.