Estimations of the isomer shifts for tetraoxoferrates

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Abstract. ⁵⁷Fe 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 nucleus 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), KFeO₄, and iron(VIII) oxide, FeO₄.

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 [FeO₄]ⁿ⁻ (n=4÷2), which give ferrate(VI)-anion, FeO₄²⁻, when come into water. FeO₄²⁻-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.

The focus of this study is the estimation of the isomer shift values on the base of non-empirical calculations for ferrate-anions in the highest oxidation degrees.

2. Calculations
To calculate the geometrical parameters of the isolated ions [FeⁿΟ₄]ⁿ⁻ (m>3) the optimization procedure at the gradient-corrected DFT level by using the three-parameter fit of the exchange-correlation potential suggested by Becke in conjunction with the LYP exchange potential [3] (B3LYP) within the GAUSSIAN’03 program [4] was applied. The use of all-electron basis set DGDZVP for all atoms is better with respect to accuracy and efficiency. The analysis of the atomic charge has been done using the NBO approach [5].

Isomer shifts in this paper are related to α-iron and are presented in [mm·s⁻¹].

3. Results and discussion
First, the geometries of ions [FeO₄]ⁿ⁻ (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: Na₄FeO₄ [6], K₂FeO₄ [8], K₃FeO₄ [10, 11]. In these compounds iron is in practically regular tetrahedral oxygen
Table 1. Calculated 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 | \( \delta_{\text{Fe-O}}^{\text{cal.}} \) mm\,s\(^{-1}\) | \( \delta_{\text{Fe-O}}^{\text{exp.}} \) mm\,s\(^{-1}\) | \( \rho_0 \) a\(_0\)\(^{-3}\) | \( N_s \), e |
|------------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| +4                     | 1.848            | 1.804            | -0.18            | -0.22            | 11617.4          | 0.223            |
|                        | for Na\(_4\)FeO\(_4\) |                  |                  |                  |                  |                  |
| +5                     | 1.736            | 1.695            | -0.55            | -0.55            | 11618.6          | 0.241            |
|                        | for K\(_3\)FeO\(_4\) |                  |                  |                  |                  |                  |
| +6                     | 1.668            | 1.640            | -0.87            | -0.90            | 11619.6          | 0.255            |
|                        | for K\(_2\)FeO\(_4\) |                  |                  |                  |                  |                  |
| +7                     | 1.619            |                  | -1.18            |                  | 11620.6          | 0.268            |
| +8                     | 1.586            |                  | -1.40            |                  | 11621.3          | 0.277            |

arrangement. The average Fe-O distances used for comparison are presented in Table 1. The correlation diagram is presented in Figure 1 and gives us very good results:

\[
R_{\text{Fe-O}}^{\text{exp.}} [\text{Å}] = -0.2 + 1.1R_{\text{Fe-O}}^{\text{cal.}} [\text{Å}] \quad (r=0.987; s=0.02; n=4)
\]

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.

The calculations showed that the increasing of the iron oxidation state (OS) lead to decreasing both natural charge on the oxygen atom (\( \Omega_0 \)) and natural charge of the iron atom (\( \Omega_{\text{Fe}} \)). The respective dependencies are described by the following correlation equations:

\[
\Omega_0 [\text{e}] = -2.5 + 0.27\text{OS} \quad (r=0.9999; s=0.007; n=5)
\]

\[
\Omega_{\text{Fe}} [\text{e}] = 1.9 - 0.08\text{OS} \quad (r=0.981; s=0.03; n=5)
\]

Rising of the oxidation state is also accompanied by the increase of the electron density on the iron nucleus (\( \rho_0 \)) (see Figure 4):

\[
\rho_0 [\text{a}_0^{-3}] = 11613.6 + 0.98\text{OS} \quad (r=0.996; s=0.16; n=5)
\]

Finally \( \rho_0 \) has been compared with experimental isomer shifts of known ferrates (Figure 5). This dependency has also good correlation parameters:

\[
\delta [\text{mm/s}] = 3635.023 - 0.3129\rho_0 [\text{a}_0^{-3}] \quad (r=0.999; s=0.02; n=3)
\]
Based on the calculated values of the electron density on the iron nucleus the obtained correlation allows us to estimate the isomer shifts for tetraoxoferrate (VII) and (VIII) (-1.18 and -1.40 mm·s⁻¹ relative to α-Fe respectively).

It will be noted that absorption lines in the respective range were already observed formerly at the spectra of Na₂FeO₄ [7]. This compound decomposes at room temperature by disproportionation mechanism. During this multistage process several higher oxidation states of iron can be observed. Interaction of Na₂FeO₄ with Na₂O₂ also allowed us to synthesized iron derivatives showing absorption lines with extremely low shifts [7]. The line with isomer shift -1.52 mm·s⁻¹ (at 78 K) was also observed in the frozen solutions, obtained by anodic dissolution of metallic iron in concentrated 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 [13]. 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 [14-16]. 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 [11]. 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 [16]. 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 depends 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:

\[
\delta \text{[mm·s}^{-1}] = -0.214 - 0.045N_\text{S}[\text{e}] \\
(r=0.999; s=0.001; n=5)
\]

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

An addition of the N₄ population increment to the last equation impairs the quality of the correlation, the standard curve fit error being 0.01 mm·s⁻¹. Thus, our calculations show that the shielding of the iron nucleus by d-electrons does not influence on the isomer shift.

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