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Does the ^{57}Fe Mössbauer isomer shift depend on the oxidation state of iron?

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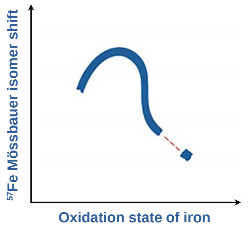
The ^{57}Fe Mössbauer isomer shift is not directly related to the oxidation state of iron, and therefore the evaluation of the oxidation state of iron from the isomer shift is problematic. The oxidation state affects the isomer shift only to the extent that it affects the Fe–X bond lengths. The isomer shift can be estimated based on the average Fe–X interatomic distance.



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Estimating the oxidation state of iron (OS$_{Fe}$) in chemical compounds using the ^{57}Fe Mössbauer isomer shift (IS) has been common practice for over 60 years. For example, Keilverth *et al.*[1] recently synthesized a series of high-valence iron nitrido complexes stabilized by the tripodal N-heterocyclic carbene ligand TIMMN^{Mes}. To confirm OS$_{Fe}$ in these complexes with iron in different oxidation states, they were studied by Mössbauer spectroscopy. It was noted that the ISs of four compounds, [LFe^{IV}(≡N)](PF$_6$) **1**, [LFe^{V}(≡N)](PF$_6$)$_2$ **2**, [LFe^{VI}(≡N)(F)](PF$_6$)$_2$ **3** and [LFe^{VII}(≡N)(F)](PF$_6$)$_2$(PF$_6$/MF$_6$) **4** (L = TIMMN^{Mes}; M = Mo, Re), which are formed from each other during successive oxidative reactions, decrease linearly with increasing OS$_{Fe}$, despite the fact that the iron atom in these compounds has a different coordination environment. At the same time, the IS of the cyclic Fe^{V} imido complex [(L*)Fe^{V}(=N*)(NCMe)](PF$_6$)$_2$(MoF$_6$) **5** (* = single bond between L and N), which is a product of the rearrangement of complex **4**, falls out of the found linear relationship.

A decrease in the value of IS with an increase in the OS$_{Fe}$ occurs frequently. For example, this is observed for alkali metal ferrates, which Keilverth *et al.*[1] used for comparison. These compounds contain tetrahedral ions $[FeO_4]^{n-}$ (n = 2–5), corresponding to OS$_{Fe}$ of +3 to +6 respectively, while ferrates(II) are unknown. Figure 1 shows a plot of IS *vs.* OS$_{Fe}$ for some selected iron oxo compounds with different OS$_{Fe}$ and different spatial structures of iron polyhedra[2] (Table S1, see Online Supplementary Materials). For ferrates this relationship is approximately linear. However, if we consider other compounds with [FeO$_4$] tetrahedra or compounds containing octahedral [FeO$_6$] fragments, the linearity disappears. It is surprising that the point for Sr$_3$Fe$_2$O$_5$ with a square planar [FeO$_4$] fragment lies on the ferrate line, but given the wide range of IS values of iron(II) compounds, this may simply be a coincidence.

From Figure 1 it is clearly seen that the dependence of the IS of iron oxo compounds on the OS$_{Fe}$ in them is not a line, but a fairly broad band. The narrowing of this band with increasing OS$_{Fe}$ is easily explained by the decrease in the number of currently known corresponding compounds. Therefore, determining the OS$_{Fe}$ of an unknown compound simply by its IS is problematic.

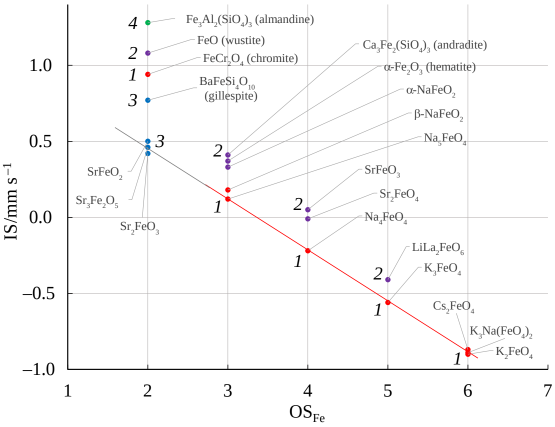

Figure 1 Dependence of the ^{57}Fe Mössbauer ISs, measured at room temperature relative to α-iron, on the OS$_{Fe}$ in selected compounds (see Table S1), in which the coordination polyhedra of iron atoms take the form of (*1*) tetrahedron, (*2*) octahedron, (*3*) a flat square or (*4*) a distorted cube.

The dependence of IS on OS$_{Fe}$ is a kind of basic knowledge written down in most current textbooks.[3–5] However, it has now been reliably established that IS does not always decrease with increasing OS$_{Fe}$. For example, in a pair of complexes $\{Fe[C(SiMe_3)_3]_2\}^{0/1-}$ ISs are close, although OS$_{Fe}$ in them are different.[6–8] Please note that this is the case where OS$_{Fe}$ can be calculated using chemical formulas! There are also examples of a systematic increase in IS with an increase in formal OS$_{Fe}$.[9] Thus, we have to see the obvious: there is no direct relationship between IS and OS$_{Fe}$.

However, let us consider the dependence of IS on OS$_{Fe}$ according to the method of Keilverth *et al.*[1] and first pay attention to the sources of uncertainty. There is uncertainty in the experimental determination of IS. For well-resolved ^{57}Fe Mössbauer spectra, it usually does not exceed several hundredths of mm s^{-1}.[10] However, there is a problem associated with the contribution of the second-order Doppler shift to the IS.

This contribution depends on the measurement temperature.[11] The higher the temperature, the greater the contribution, but it is also present at 0 K. With increasing temperature, the values of this contribution for different substances begin to converge, and its temperature dependence becomes linear. Theoretical consideration within the Debye model of a solid satisfactorily reflects the experimentally observed trends,[11] but the actual maximum value of this contribution for an arbitrary substance at different temperatures has not yet been reliably estimated.

Organoiron compounds are often unstable under ambient conditions, meaning that their Mössbauer spectra must be measured at lower temperatures. The temperature of liquid nitrogen is quite typical for this purpose. But this temperature is often outside the range in which the IS is linearly dependent on temperature. As a result, IS values can deviate by up to a tenth of mm s^{-1} or even more.

There is no uncertainty regarding OS_{Fe} in a stoichiometric compound. However, OS_{Fe} is not measured directly. It can be evaluated on the basis of chemical composition, synthetic considerations, magnetic, structural and other available data while considered together. But OS_{Fe} often cannot be assessed unambiguously. Such an assessment for compounds with unsaturated chemical bonds is not always straightforward. This should be taken into account when considering any OS_{Fe}-related dependencies.

In Figure 2, the IS points of compounds **1–5**[1] are shown as triangles. The point of compound $[(L^*)Fe^{V}(NH^*)(F)](PF_6)_3$ **6** is not shown due to the lack of Mössbauer data. The IS points of compounds **1** and **2** are connected to each other, since these complexes have similar spatial structures. Although the structure of compound **4** has not been reliably established,[1] we conventionally connected its IS point with a dashed line to the IS point of structure **3**.

As mentioned above, the iron atom in complexes **1–5** is in different oxidation states and has different coordination environments. It is therefore logical to compare their ISs with those of other organic complexes with iron in high oxidation states (see Table S2 and Figure 2, circled dots). For this purpose, pairs of points for compounds with similar composition and spatial structure were also connected to each other. It should be emphasized that the values of oxidation states were taken from original publications.

Firstly, there is a general trend of decreasing IS as OS_{Fe} increases. However, it is impossible to approximate it with a single line. The spread of ISs reaches 0.3 mm s^{-1} for iron(V) compounds and can be wider.[12] Therefore, if, for example, the point of complex **4** is moved in the row for iron(VI) compounds, the general dependence will not be violated.

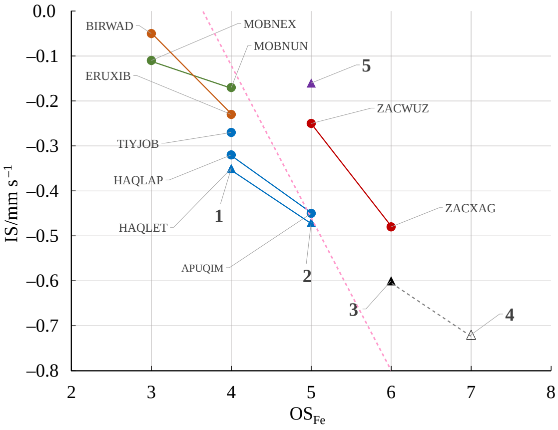

Figure 2 Dependence of the ^{57}Fe Mössbauer ISs, measured at liquid nitrogen temperature relative to α-iron at room temperature, on the OS_{Fe} in selected organoiron compounds (Table S2). Symbols of the same color correspond to compounds that are similar in structure. The pink dashed line corresponds to the ferrates.

Secondly, the slope of the straight line passing through the points for complexes **1–4** is small and clearly less than the slope of a similar straight line for ferrates (−0.33 mm s^{-1}).[13] For other pairs of structurally related compounds, the slopes differ. The small slopes can be explained by the uncertainties mentioned above.

Thirdly, pairs of compounds with similar structures and different OS_{Fe} are visible, but triads or tetrades, as in the case of ferrates, are not observed. This allows us to assume the existence of non-integer OS_{Fe} to interpret the observed picture.[14] The slight slopes of the IS–OS_{Fe} lines may also support this interpretation.

Finally, note that the IS point of compound **4** in Figure 2 lies on the same straight line as the pair of points of ZACWUZ and ZACXAG. Can this be considered a confirmation of the heptavalency of iron in compound **4**?

Thus, the estimation of OS_{Fe} in a pair of compounds **3** and **4** by comparing them with another pair of compounds **1** and **2**, based on the possibility of linearizing their points on the IS–OS_{Fe} plot despite differences in the composition and geometry of iron coordination polyhedra and other specified circumstances, appears to be ephemeral.

One of the reviewers of this article pointed out that predicting IS through DFT calculations is current and usual way. That would be great. There are currently over a million organic structure entries in the CCDC database,[15] about 4–5% of which relate to iron compounds. It would be amazing if we could calculate the Mössbauer parameters for all of them by extracting the structural data from the database and processing them automatically. Among the more than five thousand known minerals, there are more than a thousand iron minerals.[16] It would be helpful to have a list of predicted ISs for them. But fully validated algorithms (IS calculators) suitable for direct practical use are not available today. The number of DFT-based Mössbauer studies remains in a clear minority (Figure S1, see Online Supplementary Materials).

Neese[17] summarized the approach to estimating IS using DFT calculations: ‘The theoretical approach is to simply construct a linear plot between theoretically predicted electron density at the Fe nucleus (ρ_0) and experimentally measured ISs.’ As we can see from previous works,[18,19] this general strategy remains unchanged. It is important that the specified plot, characterized by the slope of a straight line, called the ‘calibration constant’, does not show any trends associated with the observed properties of the substance:[17] ‘The correlation appears to be independent of the total charge, valence state, spin state, coordination number and coordination geometry.’

Keilverth *et al.*[1] performed extensive calculations. However, they did not present either the calibration curve (IS–ρ_0 plot) or the result of the IS calculations. But it would seem that this should be done on the basis of known structural data for complexes **1–3**, **5** and **6**, as well as on the basis of the proposed structure of complex **4** (as was done, for example, in previous work[20].) Instead, the calculation result is presented in an atypical way.[1] Should we conclude that the usual calculation format did not produce a suitable result?

Neese[5] estimated the uncertainty in determining IS using a calibration constant to be 0.1 mm s^{-1}, although this value is clearly somewhat higher than in other relevant works.[18,19] At the same time, if ρ_0 is calculated and correlated with the experimental IS, then uncertainty will arise due to the contribution of the second-order Doppler shift, which is not associated with the change in ρ_0. Therefore, the calculation of this component must be performed additionally.

Calculations make it possible to obtain the IS value based on data on the structure of a substance. However, from a practical point of view, the inverse problem of calculating the properties of a substance from the measured IS is also relevant. For practical purposes, it would be beneficial to have a simple and easy-to-understand algorithm that could provide chemical information (perhaps too precise) based on the measured IS and that could estimate the IS based on other experimental data. Therefore, it is appropriate to consider a simple empirical approach that relates the observed IS values to the structural and other parameters of substances.[13,21]

For the substances studied by Keilverth *et al.*,[1] at least two factors affecting IS should be considered.[2] The first factor is the average interatomic distance Fe–X (aID$_{\text{Fe–X}}$), where X denotes an atom of any element in the first coordination sphere of the iron atom). The second factor is associated with the introduction of an additional atom into the coordination polyhedron of the iron atom. According to the approach,[2] IS tends to decrease with the incorporation of certain ligands into the coordination polyhedron of the iron atom. Specifically, an increase in the coordination number of iron in oxides leads to a decrease in the IS when comparing the IS values for any selected aID$_{\text{Fe–O}}$.[2]

Figure 3 presents dependence of IS on aID$_{\text{Fe–X}}$ for the compounds studied in the cited work.[1] The IS point of fluorine-containing compound **3** lies below the line of fluorine-free compounds **1** and **2**. Compound **5** contains an additional acetonitrile ligand, which may not contribute much to the IS (compare data for OROTEV with data for WIVLUK and OROSOE[21]). Therefore, the IS point of compound **5** lies close to the line of compounds **1** and **2**. Since compounds **4** and **6** lack either structural or Mössbauer data, respectively (see Table S2), they cannot be represented in Figure 3. But using the IS value of compound **4** and the interatomic distances in compound **6**, one can try to predict the structural or Mössbauer parameters, respectively. This can be done based on the location of points for substances related in structure and composition of iron polyhedra (see Figure 3).

If the structure of fluorine-containing iron(VII) compound **4** is similar to the structure of compound **3**, their points should lie close to the same line with a slope of 0.04 mm s^{-1} pm^{-1}. The Fe–F distance in compound **6** is significantly longer, and the distance between iron and the second nitrogen is shorter. Thus, the average distance can be calculated in different ways. However, as a first approximation, it is reasonable to expect the IS value of compound **6** to be around −0.4 mm s^{-1} or slightly higher.

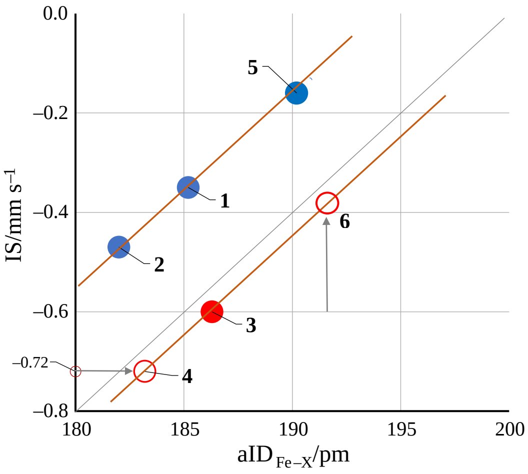

Figure 3 Relationship between ^{57}Fe Mössbauer ISs, measured at liquid nitrogen temperature relative to α-Fe at room temperature, and aID$_{\text{Fe–X}}$ in known compounds.[1] The sizes of the circles approximately correspond to 0.04 mm s^{-1} and 1 pm. The expected positions of the circles for compounds **4** and **6** are also shown.

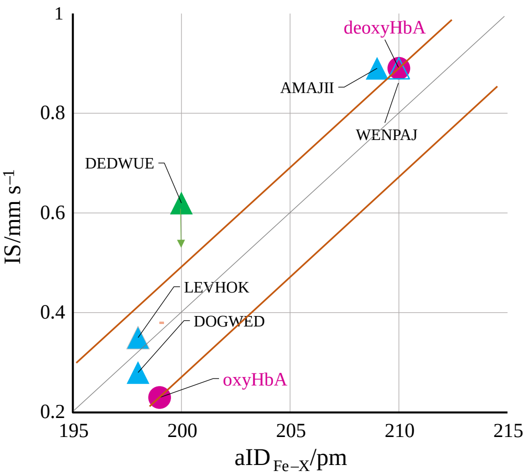

Figure 4 Relationship between ^{57}Fe Mössbauer ISs, measured at liquid nitrogen temperature relative to α-Fe at room temperature, and aID$_{\text{Fe–X}}$ in hemoglobin (magenta circles) and some related compounds. The green triangle corresponds to IS measured at 4 K and should therefore be moved downwards.

The effect of introducing a fluorine atom into the iron polyhedron[1] is reminiscent of the change in the IS of hemoglobin as a result of the conversion of the deoxy form to the oxy form or the binding of a CO molecule. Figure 4 shows the points of oxy- and deoxy-hemoglobin in IS–aID$_{\text{Fe–X}}$ coordinates (Table S4). The addition of a gas molecule by hemoglobin leads to a decrease in aID$_{\text{Fe–X}}$.[22] This should reduce the IS along a line with a slope of 0.04 mm s^{-1} pm^{-1}. An additional drop of IS associated with the appearance of oxygen in the coordination sphere of iron should also be observed. And this is exactly what we see in Figure 4, which uses the average aID$_{\text{Fe–X}}$ values for all subunits.[23,24] The CO-HbA point coincides with the Oxy-HbA point. To support the interpretation, Figure 4 also shows the points of several other porphyrin iron complexes listed in Table S4.[25–30]

The presented empirical approach to estimating IS does not take OS$_{\text{Fe}}$ into account. The Fe–X interatomic distances are determined by a combination of the OS$_{\text{Fe}}$, the spin of the iron atom (ion), the spatial structure of its coordination polyhedron and also the size (radius) of the X atom (ion). This is clearly seen, for example, from the table of crystallographic (ionic) radii.[31,32] Thus, in essence, aID$_{\text{Fe–X}}$ accumulates all these factors.

Like other approaches, this one also has a number of uncertainties. The IS is sensitive to structural parameters, since an uncertainty in the determination of aID$_{\text{Fe–X}}$ of 1 pm corresponds to an uncertainty in the determination of the IS of 0.04 mm s^{-1}. Uncertainty may increase if the Fe–X bond lengths in the iron polyhedron vary significantly. In addition, the above-mentioned uncertainty associated with the measurement temperature is also significant.

Although this approach is empirical, it has a theoretical foundation. It is also consistent with the theoretical conclusion that ‘the iron–ligand bond lengths play a decisive role for the isomer shift of a compound’.[5] By considering the coefficient of 0.04 mm s^{-1} pm^{-1}, which can be easily found from the results of DFT calculations, in combination with the calibration constant, we may be able to better understand this role.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mendcom.2024.09.002.

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