DFT calculations of ^{57}Fe Mössbauer parameters for [FeFe]-hydrogenase models

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Introduction: ^{57}Fe Mössbauer spectroscopy is ideally suited for the study of active site of metallo-enzymes containing iron atoms, since it provide parameters reflecting the geometric and electronic structures of metalloproteins along reaction pathways. This specialized spectroscopic method can be also applied to synthetic compounds to investigate the oxidation state of iron atoms.

Aim of the work: to resolve the ambiguities in the assignment of the red-ox state of the iron atoms in the [FeFe]-hydrogenase active site and its biomimetic models, we compare experimental data with isomer shifts (δ) and quadrupole splitting (ΔE_Q) parameters calculated with quantum-mechanical method. We predicted Mössbauer parameters for few [FeFe]-hydrogenase biomimetic compounds, in the formal Fe^{I}Fe^I and Fe^{II}Fe^I states. Comparison of δ for complexes with different ligands allow to better rationalize the steroelectronic features required for the design of novel biomimetic catalysts.

Isomer shifts of iron compounds

$$\delta = C \left\{ |\Psi(0)|_A^2 - |\Psi(0)|_S^2 \right\} (R_e^2 - R_g^2)$$

$C = (2/3)\pi Z e^2$

$\{|\Psi(0)|_A^2 - |\Psi(0)|_S^2\}$ = electron density at the nucleus of an absorber relative to a given source

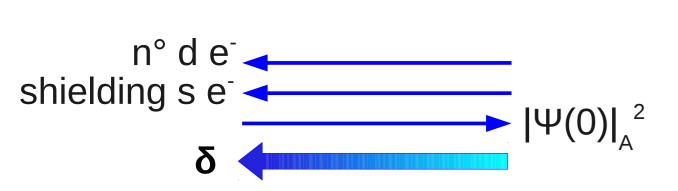R_e, R_g = nuclear radius in excited and ground state

For a given atom and the same source

$$\delta = C' \left\{ |\Psi(0)|_A^2 \right\}$$

For ^{57}Fe $(R_e^2 - R_g^2) < 0$

Increase of $|\Psi(0)|_A^2$ ⟹ δ more negative

$Fe^+(3d^7) > Fe^{2+}(3d^6) > Fe^{3+}(3d^5)$

n° d e$^-$
shielding s e$^-$ → $|\Psi(0)|_A^2$
δ

Comparison of experimental and calculated Mössbauer parameters of iron atoms in [2Fe]$_H$ complexes
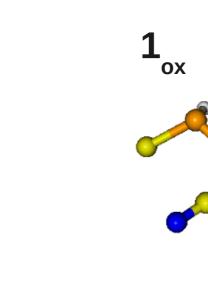
δ is proportional to $|\Psi(0)|_A^2 \equiv \rho(0)_A$ which is easily calculated by DFT. We can therefore consider the simple equation:

$\delta = a[\rho(0)_A - c] + b$

where a, b = fitting parameters to be determined by linear regression
c = number that is merely introduced for convenience

In this work δ is predicted with B3LYP functional and equation [1]
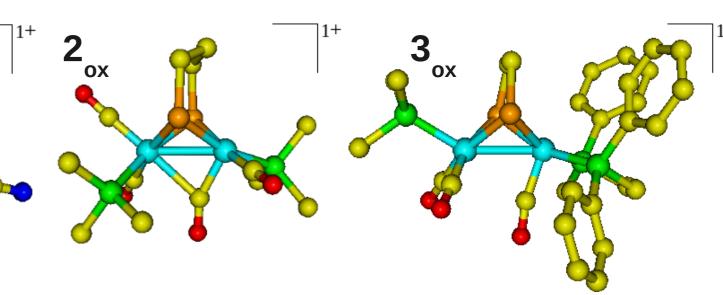$\delta = -0.298 [\rho(0)_A - 11580] + 1.118$

Figure 1: biomimetic compounds, computed at DFT-BP86/TZVP level of theory.

Table 1: experimental (red, italic) and predicted Mössbauer parameters of iron atoms of H-cluster and of compounds 1, 2, 3.
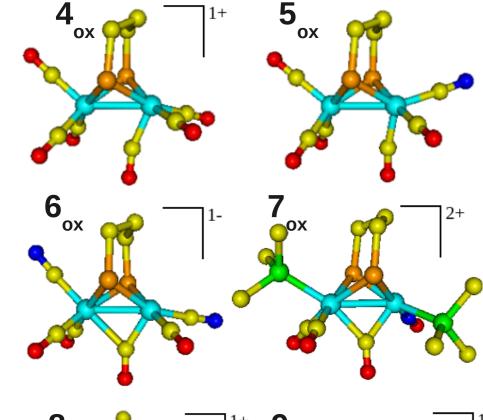
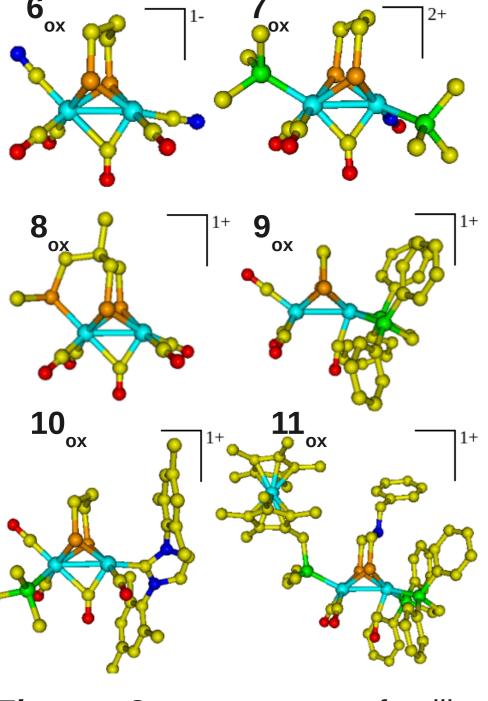|		Hred [2]	Hox [2]	1	1ox	2 [3]	2ox [3]	3	3ox [4]
δ (mm/s)	Fep	*~0.08*	*0.1<δ<0.3*	0.21	0.21	0.05 / *0.06/0.06*	0.10 / *0.10*	0.05	0.07 / *0.04*
	Fed			0.03	0.14	0.05 / *0.07/0.06*	0.17 / *0.19*	0.21	0.25 / *0.20*
ΔE_Q (mm/s)	Fep	*~0.87*	*0.7< ΔEQ <1.2*	0.46	1.02	-0.96 / *-1/1.33*	0.79 / *0.55*	-0.94	0.66 / *0.70*
	Fed			-1.01	0.86	-0.84 / *0.75/0.85*	-0.73 / *1.06*	-0.81	0.41 / *-0.58*

Parameters of 2 and 3 match very well the experimental values, suggesting that the computational scheme is able to correctly describe the electronic structure of this type of complexes.
Experimental parameters of the enzyme are not well reproduced, probably due to the model 1, that not include the [Fe$_4$S$_4$] cluster.
Contrary to the expected, δ increase with oxidation of [2Fe]$_H$ site.

Prediction of Mössbauer parameters for biomimetics compounds with different ligands

Figure 2: geometry of diiron models investigated

Table 2: δ, calculated with B3LYP functionals, and charge of Fe fragments of complexes 2-11.

	δ (mm/s)			q		
	Fep	Fed	Δδ	Fep	Fed	Δq
2	0.05	0.05	0.00	0.10	0.11	-0.01
2ox	0.10	0.17	-0.07	0.66	0.49	-0.17
3	0.05	0.21	-0.16	0.07	0.28	-0.21
3ox	0.07	0.25	-0.18	0.55	0.70	-0.15
4	-0.01	-0.01	0.00	0.04	0.05	-0.01
4ox	0.05	0.13	-0.08	0.52	0.39	0.13
5	-0.02	0.00	-0.02	-0.22	-0.52	0.30
5ox	0.00	0.04	-0.04	0.22	-0.21	0.43
6	0.01	0.02	-0.01	-0.78	-0.82	0.04
6ox	0.05	0.10	-0.05	-0.36	-0.42	0.06
7	0.06	0.07	-0.01	0.59	0.56	0.03
7ox	0.15	0.18	-0.03	0.90	1.01	-0.11
8	0.11	-0.02	0.13	0.24	-0.02	0.26
8ox	0.18	0.17	0.01	0.70	0.37	0.33
9	-0.03	0.20	-0.17	-0.14	0.36	0.50
9ox	0.01	0.23	-0.22	0.31	0.78	-0.47
10	0.06	0.08	-0.02	0.16	0.14	0.02
10ox	0.11	0.17	-0.06	0.58	0.58	0.00
11	0.12	0.24	-0.12	0.18	0.27	-0.09
Fc	0.66					
11ox	0.12	0.27	-0.15	0.99	0.31	0.68
Fc	0.67					

Chemical bond properties

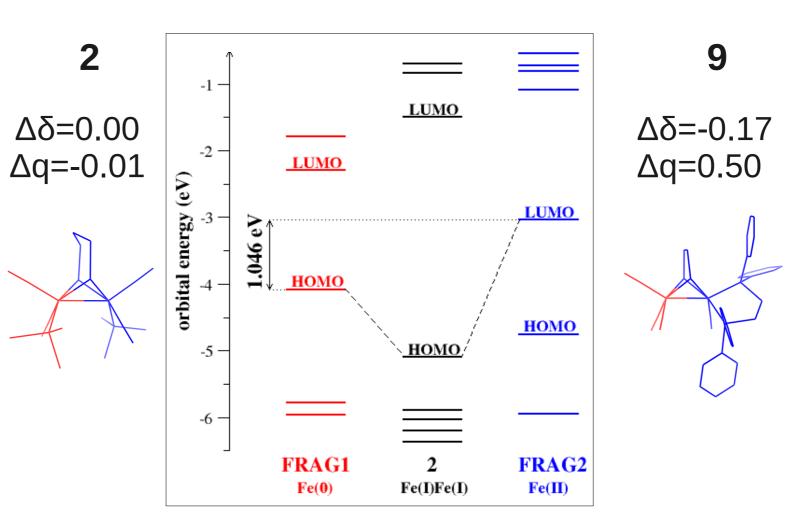$S^{2-} > P(Me)_3 > P(Ph)_3 > CN^- > CO > NO^+$

δ ← → π backbonding

Discussion

- In the reduced state only few compounds are characterized by significantly different δ at two iron atoms.
- Desymmetrization of the complex by using different ligands not always correspond to a differentiation in δ at iron nuclei.
- Except for complex 5, $\Delta\delta$ can be correlated to the charge difference (Δq) between the two Fe fragments.
- Δq can be explained considering the orbital diagram of two neutral subunits, which feature the formal Fe^{II} and Fe^0 redox states. Formation of the bimetallic cluster from the two fragments can be described by a donor-acceptor interaction between occupied orbitals of the Fe^0 fragment and unoccupied orbitals of the Fe^{II} fragment to give Fe^{I}Fe^I complex.
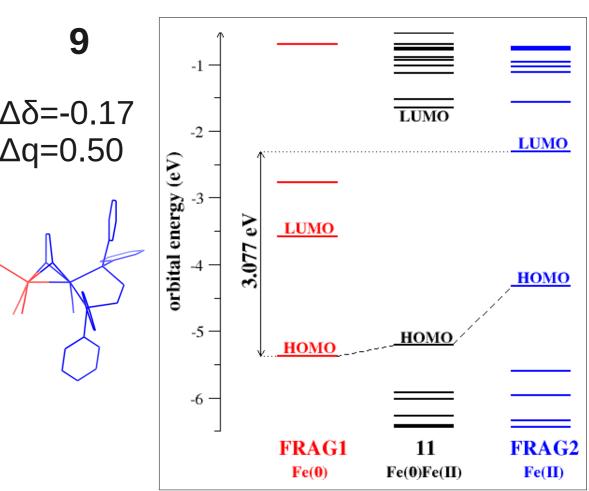

Figure 3: orbital energy diagram of the complexes 2 and 9 and their two subunits.

Large $\Delta\delta$ between the two iron atoms is indicative of the biomimetic complex desymmetrization. Calculation of Mössbauer parameters can then be a preliminary step in design of novel catalysts.

References

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