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

Raffaella Breglia$^a$, Luca De Gioia$^b$, Claudio Greco$^a$, Maurizio Bruschi$^a$

$^a$ Department of Earth and Environmental Sciences, University of Milano-Bicocca, Piazza della Scienza 1, 20126, Milano, Italy.
$^b$ Department of Biotechnology and Biosciences, University of Milano-Bicocca, Piazza della Scienza 2, 20126, Milano, Italy.

**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 ($\delta$) and quadrupole splitting ($\Delta E_Q$) parameters calculated with quantum-mechanical method. We predicted Mössbauer parameters for few [FeFe]-hydrogenase biomimetic compounds, in the formal Fe$^{II}$/Fe$^{II}$ states. Comparison of $\delta$ for complexes with different ligands allow to better rationalize the stereoelectronic features required for the design of novel biomimetic catalysts.

**Chemical bond properties**

\[ S^2 > P(\text{Me})_3 > P(\text{Ph})_3 > \text{CN} > \text{CO} > \text{NO}^+ \]

**Discussion**

- In the reduced state only few compounds are characterized by significantly different $\delta$ at two iron atoms.
- Desymmetrization of the complex by using different ligands not always correspond to a differentiation in $\delta$ at iron nuclei.
- Except for complex 5, $\Delta\delta$ can be correlated to the charge difference ($\Delta q$) between the two Fe fragments.
- $\Delta q$ can be explained considering the orbital diagram of two neutral subunits, which feature the formal Fe$^{II}$ and Fe$^{II}$ 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$^{II}$ fragment and unoccupied orbitals of the Fe$^{II}$ complex to give Fe$^{II}$/Fe$^{II}$ complex.

**References**