

Structure of Iron Oxides FeO_n with High Oxygen Content

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Objectives

The aim of this study is to understand capabilities of iron atoms for binding multiple oxygen species (O , O_2 , and O_3). Subtasks include:

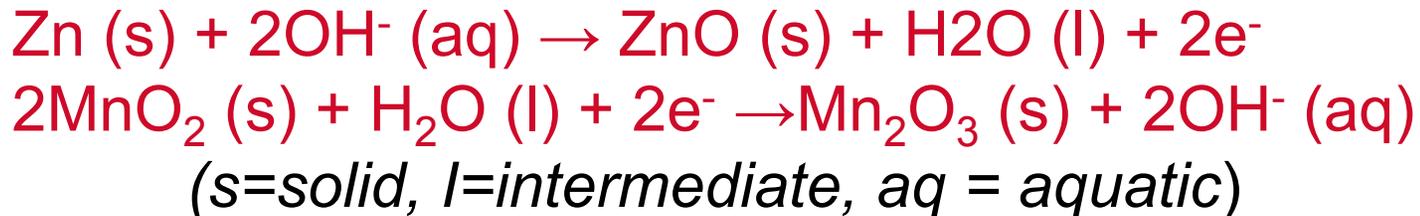
- ◆ How many oxygen units can bind to a Fe atom;
- ◆ Structure and geometrical stability of monoiron oxides;
- ◆ What is the electron affinity of FeO_n ? Are the FeO_n^- anions candidates for fabricating new materials with high oxygen content?
- ◆ What is the thermodynamic stability of neutral and singly negatively charged monoiron oxides?

Background of Problem

- High-capacity batteries were fabricated using K_2FeO_4 and BaFeO_4 as cathodes and Zn as anode (Science 285, 1039 (1999)).
- Salts containing FeO_4 and sodium ferrate Na_4FeO_5 are good oxidizers and are used for environmental purification purposes.
- FeO_6 octahedra were observed in a number of inorganic salts. In particular, clusters $\text{Fe}(\text{H}_2\text{O})_6$ are building blocks in the $\text{K}_2[\text{Fe}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ salt.

Energetic Super-Iron Battery

In Fe-based batteries, metallic Zn is an anode and KOH is an electrolyte as in conventional (not rechargeable) alkaline batteries that have MnO_2 as a cathode. The half-reactions in alkaline batteries are:



The super-iron are rechargeable batteries provide > 50% more energy capacity. The super-iron battery discharge proceeds as



At higher oxygen content, more charge carriers OH^- can be produced

Technical Approach

- Gaussian 03 program was used. For the atomic orbitals, we have used the standard contracted 6-311+G(3df) basis: **10s7p4d3f1g** for Fe and **5s4p3d1f** for O atoms.
- The primary exchange-correlation functional is comprised of the Becke's exchange and Perdew-Wang's correlation (BPW91).
- A number of DFT and hybrid HF-DFT functionals were tested.
- Each optimization was followed by computations of harmonic vibrational frequencies in order to confirm that the optimization arrived at a stationary point on the potential energy surface.

Computation quality

In order to test reliability of the BPW91/ 6-311+G(3df) approach we compared the results of our computations with experimental data.

Spectroscopic constants of O₂:

BPW91: $r_e = 1.218 \text{ \AA}$ $\omega_e = 1557 \text{ cm}^{-1}$

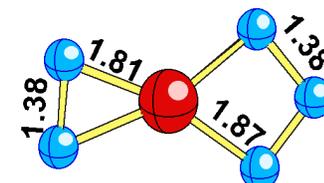
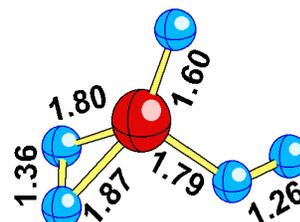
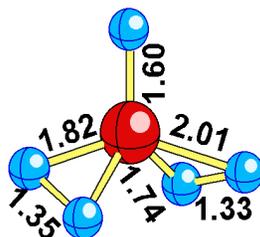
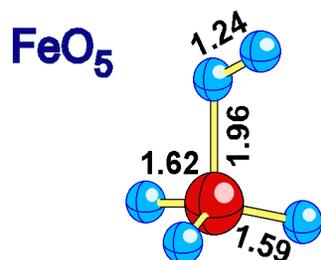
Experiment: $r_e = 1.207 \text{ \AA}$ $\omega_e = 1563 \text{ cm}^{-1}$

Electron affinity:

	BPW91	Experiment
O ₂	0.405 eV	0.448 ± 0.006 eV
FeO ₃	3.25 eV	3.31 ± 0.06 eV
FeO ₄	3.69 eV	3.84 ± 0.04 eV

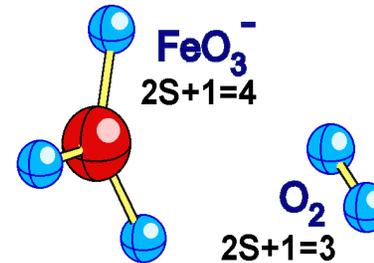
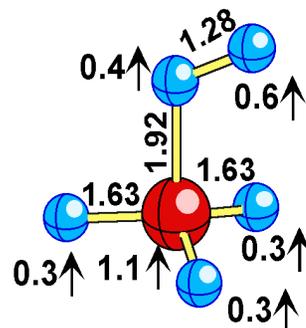
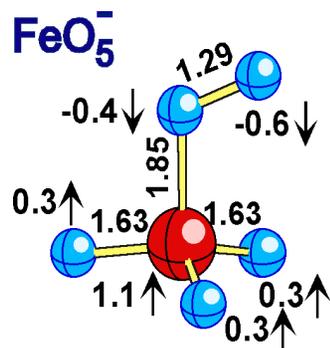
Structures of FeO_5 and FeO_5^-

There are a large number of states that are close in total energy



Singlet	0.0 eV	+0.70 eV	+0.92 eV	+1.90 eV
Triplet	+0.03 eV	+0.66 eV	+0.80 eV	+1.72 eV
Quintet	+0.83 eV	+0.74 eV	+1.03 eV	+1.58 eV

Iron atom carries a magnetic moment



$$2S+1=2$$

$$-3.99 \text{ eV}$$

$$2S+1=4$$

$$-3.72 \text{ eV}$$

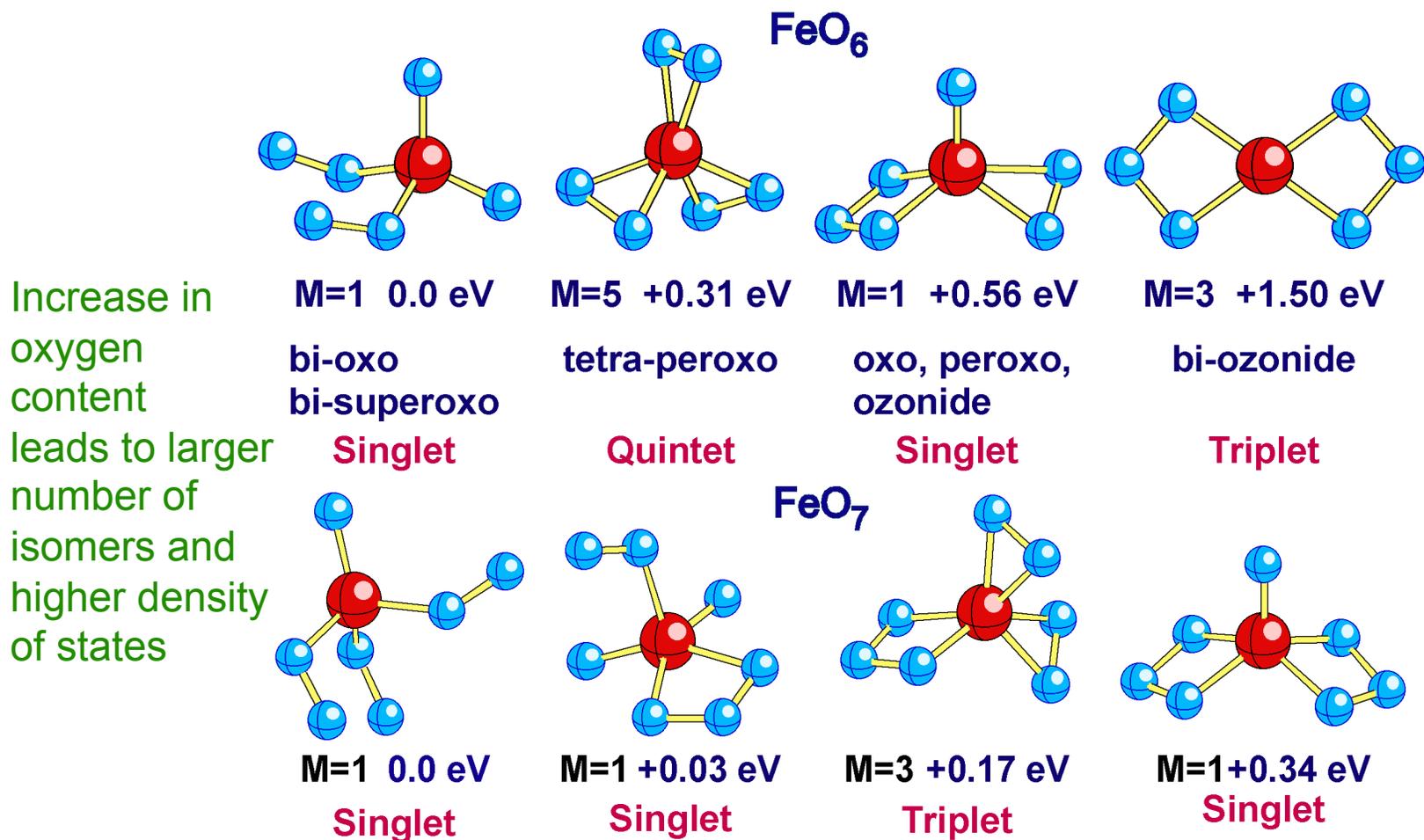
$$2S+1=6$$

$$-3.12 \text{ eV}$$

Local magnetic moments in Bohr Magnetons.
Bond lengths are in Angstroms.

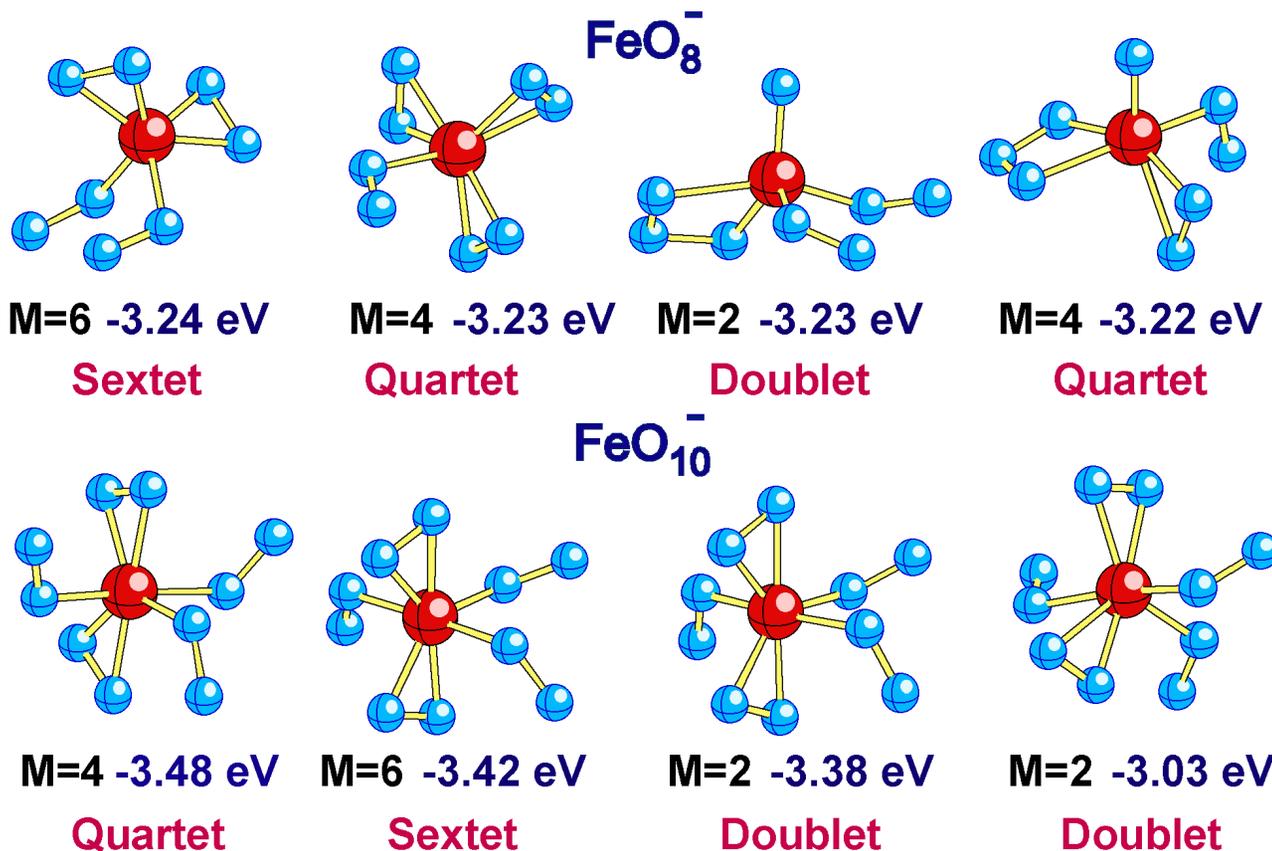
An example of spin-induced dissociation in the FeO_5^- anion

Competition of oxo, peroxy, superoxo and ozonide groups in neutral FeO_6 and FeO_7



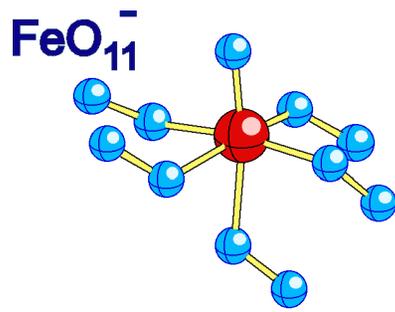
Generally, the presence of ozonide groups leads to higher total energy

The lowest total energy configurations of FeO_8^- and FeO_{10}^-

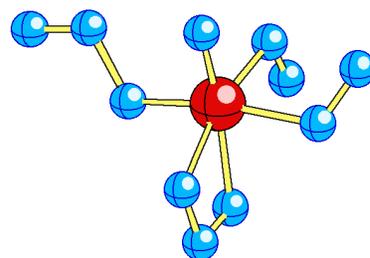


The largest number of closely spaced states are found for $n = 8$ and 9 . At larger n , the number of possible isomers sharply decreases. No O rings beyond three-atom ozonides are found.

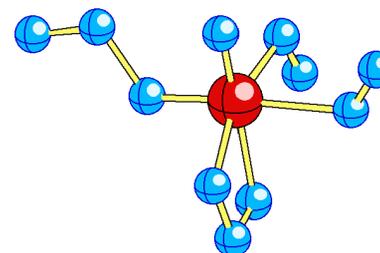
The lowest total energy configurations of FeO_{11}^- and FeO_{12}^-



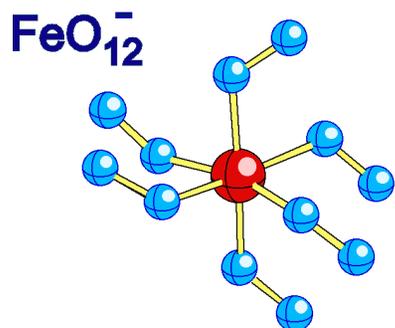
M=2 -3.62 eV
Doublet



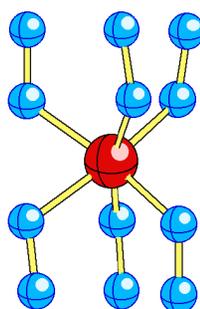
M=4 -3.22 eV
Quartet



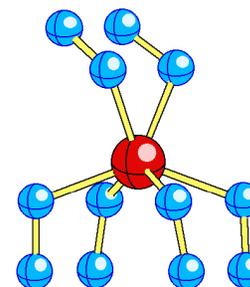
M=6 -2.93 eV
Sextet



M=6 -3.69 eV
M=4 -3.64 eV



M=6 -3.65 eV
M=4 -3.61 eV



M=4 -3.50 eV
M=6 -3.41 eV

A few geometrically stable configurations are found for $n=11$ and $n=12$. The preferred configuration for FeO_{12} is composed of 6 peroxo group. Geometrically stable states for FeO_{12} and its anion do exist up to spin multiplicities $M=2S+1 = 12$.

Adiabatic electron affinities of FeO_n computed at the BPW91 level of theory using two basis sets.

EA(F)= 3.40 eV
EA(Cl)=3.62 eV

	6-311+G*	6-311+G(3df)
FeO ₃	3.33	3.25 ^a
FeO ₄	3.79	3.69 ^b
FeO ₅	4.15	3.95
FeO ₆	3.78	3.56
FeO ₇	3.59	3.57
FeO ₈	3.54	3.24
FeO ₉	3.85	3.50
FeO ₁₀	3.52	3.48
FeO ₁₁	3.84	3.80
FeO ₁₂	3.76	3.69

All values are in eV.

^a Experimental value is 3.31 ± 0.06 eV (adiabatic).

^b Experimental value is 3.84 ± 0.04 eV (vertical).

Some FeO_n behaves as halogens and some as weak superhalogens. All of them are capable to serve as counterions in salts.

Dissociation Energies of FeO_n Through Different Decay Channels (in eV)

Channel	D ₀	Channel	D ₀
FeO ₄ → FeO ₂ + O ₂	1.88	FeO ₉ → FeO ₇ + O ₂	0.15
→ FeO ₃ + O	3.21	→ FeO ₆ + O ₃	1.17
FeO ₅ → FeO ₃ + O ₂	0.03	FeO ₁₀ → FeO ₈ + O ₂	-0.01
→ FeO ₂ + O ₃	3.11	→ FeO ₄ + 3O ₂	-0.93
FeO ₆ → FeO ₄ + O ₂	-0.50	→ FeO ₉ + O	2.76
→ FeO ₅ + O	2.68	FeO ₁₁ → FeO ₉ + O ₂	-0.69
FeO ₇ → FeO ₅ + O ₂	-0.65	→ FeO ₄ + 2O ₂ + O ₃	0.04
→ FeO ₄ + O ₃	0.58	→ FeO ₈ + O ₃	0.96
FeO ₈ → FeO ₆ + O ₂	-0.42	FeO ₁₂ → FeO ₁₀ + O ₂	-0.56
→ FeO ₄ + 2O ₂	-0.92	→ FeO ₄ + 4O ₂	-1.48
→ FeO ₇ + O	2.91	→ FeO ₁₁ + O	2.89

All FeO_n with n>4 are metastable. There are a number of exothermic channels for each n>5, the final decay products consist of FeO₄ and O₂ if n is even or O₂ and ozone O₃ if is odd.

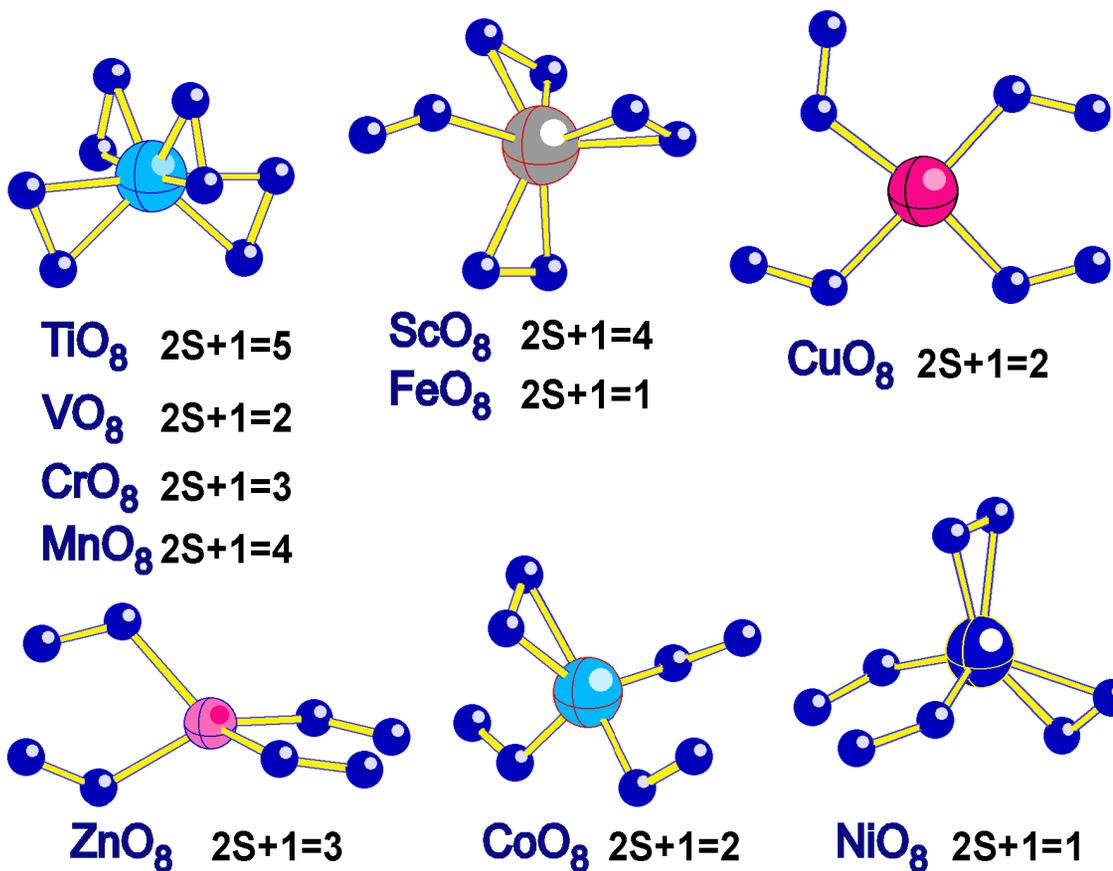
Summary

G. L. Gutsev, C. A. Weatherford, K. Pradhan, P. Jena, J. Phys. Chem. A **114** (34), 9014–9021 (2010).

The results of our computations performed using density functional theory with generalized gradient approximation (DFT-GGA) for the neutral and negatively charged FeO_n species show that there are geometrically stable isomers for each n in the range from $n = 5$ to 12.

The isomer states do correspond to local minima and are unstable toward release of dioxygen for $n > 5$. All the neutral species do possess rather large electron affinities ranging from 3.24 eV to 3.95 eV and the anions can potentially serve as counterions in salts if a proper cation is found. Such salts would possess a high oxidative power.

First results on highly rich oxides of other 3d-metal atoms



Competition between peroxo- and superoxo- O_2 in the lowest energy states of MO_8 ($M=\text{Sc-Zn}$)