

Structure of Iron Oxides FeO_n with High Oxygen Content

Charles A. Weatherford⁺ and Gennady L. Gutsev^{*}

Department of Physics
and

Center for Plasma Science and Technology
Florida A&M University
Tallahassee, Florida 32307

SPONSORS:

⁺NSF CREST

^{*}Defense Threat Reduction Agency

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:

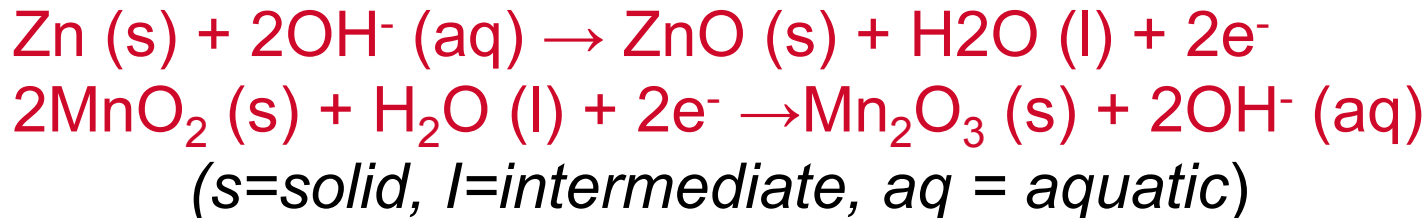
- ◆ How many oxygen units can bind to a Fe atom;
- ◆ Structure and geometrical stability of monoiron oxides;
- ◆ What is the electron affinity of FeO_n ? Are the FeO_n^- anions candidates for fabricating new materials with high oxygen content?
- ◆ What is the thermodynamic stability of neutral and singly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

Background of Problem

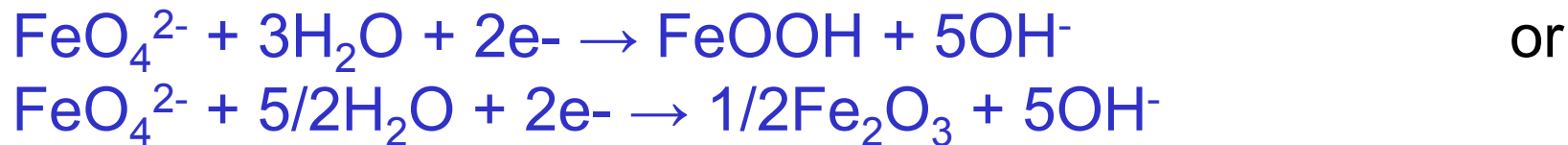
- High-capacity batteries were fabricated using K_2FeO_4 and BaFeO_4 as cathodes and Zn as anode (Science 285, 1039 (1999)).
- Salts containing FeO_4 and sodium ferrate Na_4FeO_5 are good oxidizers and are used for environmental purification purposes.
- FeO_6 octahedra were observed in a number of inorganic 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: $r_e = 1.218 \text{ \AA}$ $\omega_e = 1557 \text{ cm}^{-1}$

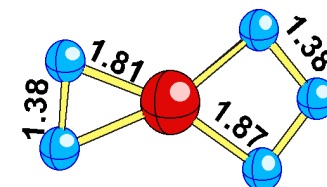
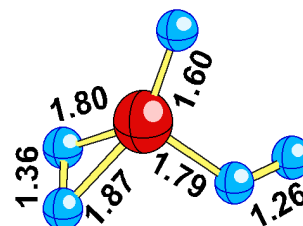
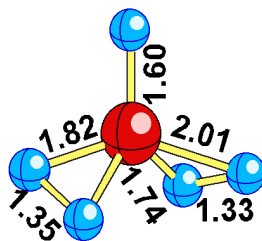
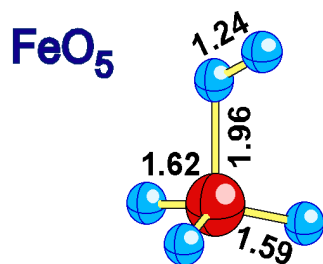
Experiment: $r_e = 1.207 \text{ \AA}$ $\omega_e = 1563 \text{ cm}^{-1}$

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

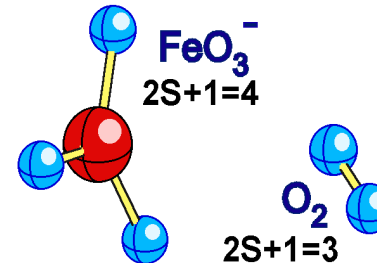
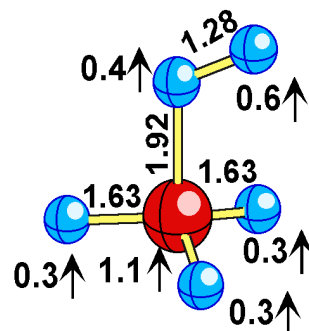
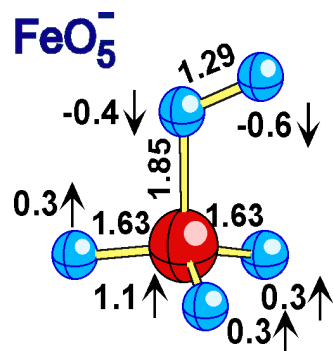
Structures of FeO_5 and FeO_5^-

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 eV

$2S+1=4$
-3.72 eV

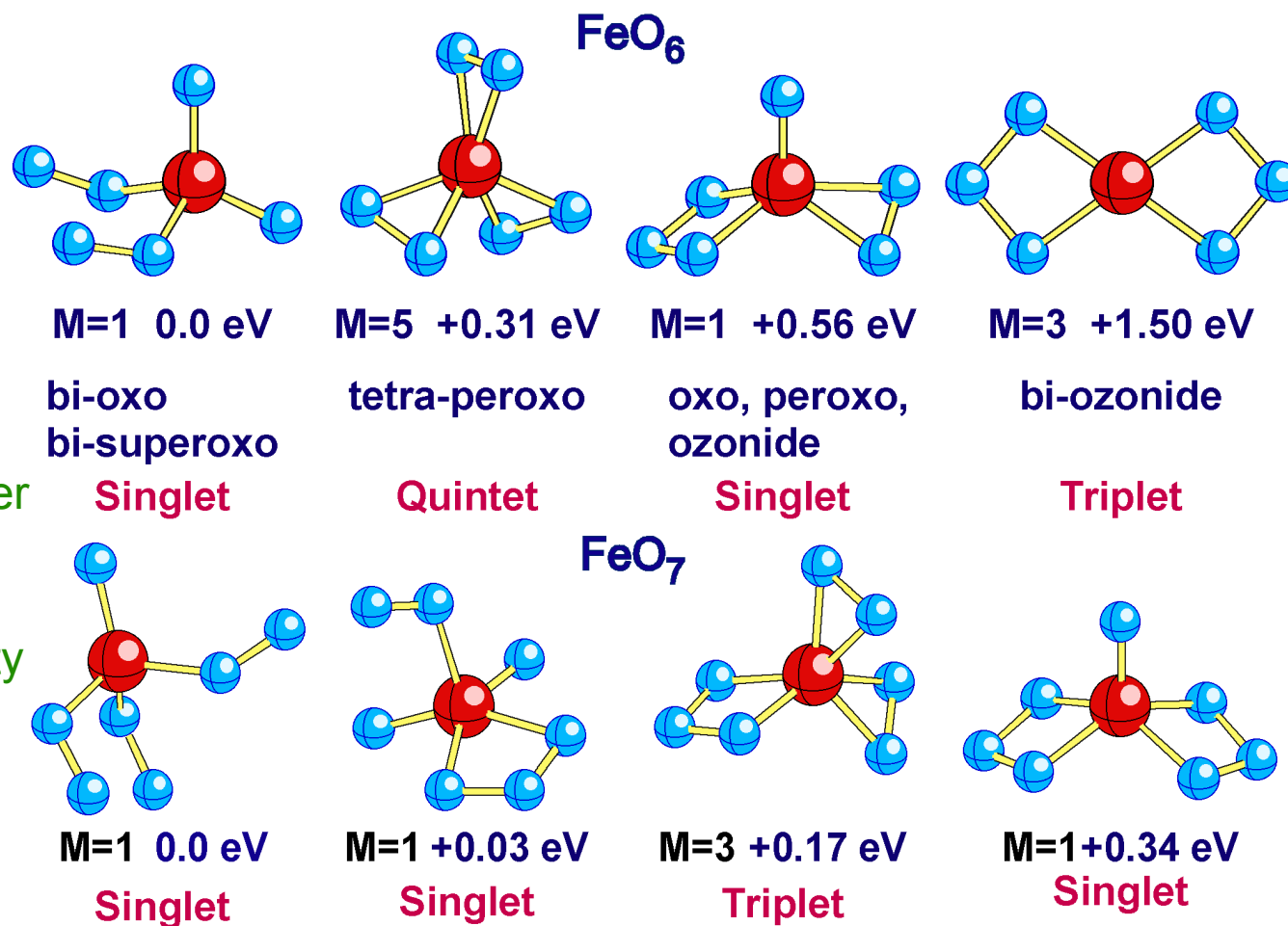
$2S+1=6$
-3.12 eV

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

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

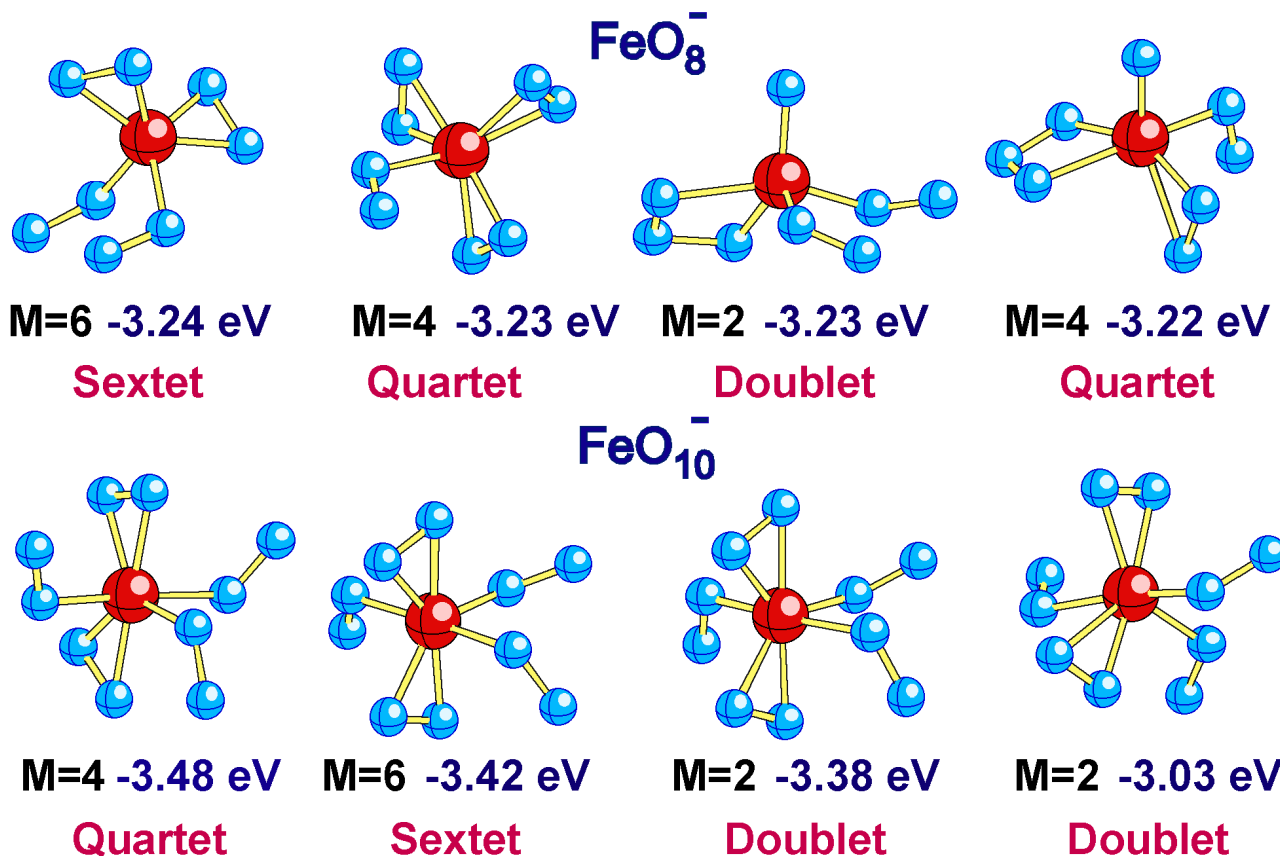
Competition of oxo, peroxo, superoxo and ozonide groups in neutral FeO_6 and FeO_7

Increase in oxygen content leads to larger number of isomers and higher density of states



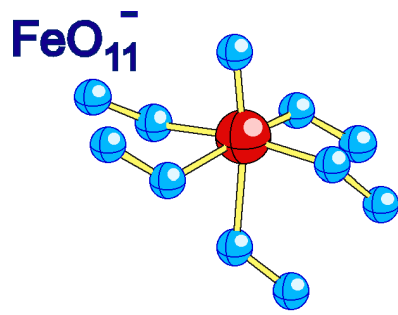
Generally, the presence of ozonide groups leads to higher total energy

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

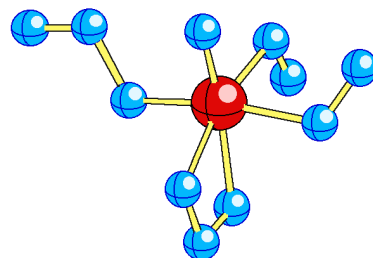


The largest number of closely spaced states are found for $n = 8$ and 9 . At larger n , the number of possible isomers sharply decreases. No O rings beyond three-atom ozonides are found.

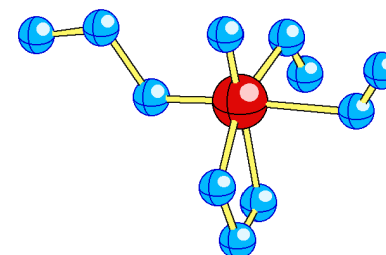
The lowest total energy configurations of FeO_{11}^- and FeO_{12}^-



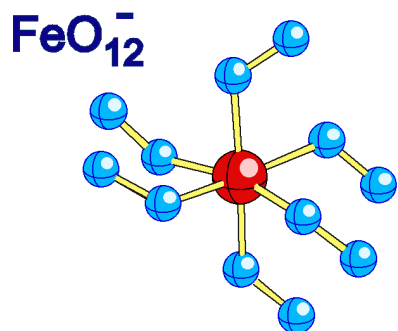
M=2 -3.62 eV
Doublet



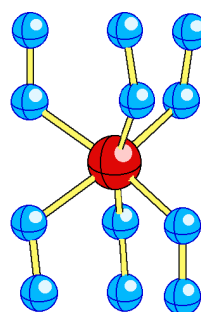
M=4 -3.22 eV
Quartet



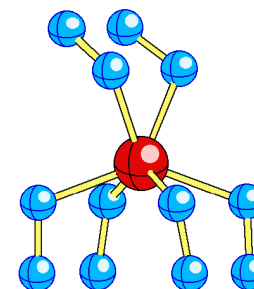
M=6 -2.93 eV
Sextet



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
FeO₄ → FeO ₂ + O ₂	1.88	FeO₉ → FeO ₇ + O ₂	0.15
→ FeO ₃ + O	3.21	→ FeO ₆ + O ₃	1.17
FeO₅ → FeO ₃ + O ₂	0.03	FeO₁₀ → FeO ₈ + O ₂	-0.01
→ FeO ₂ + O ₃	3.11	→ FeO ₄ + 3O ₂	-0.93
FeO₆ → FeO ₄ + O ₂	-0.50	→ FeO ₉ + O	2.76
→ FeO ₅ + O	2.68	FeO₁₁ → FeO ₉ + O ₂	-0.69
FeO₇ → 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
FeO₈ → FeO ₆ + O ₂	-0.42	FeO₁₂ → 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.

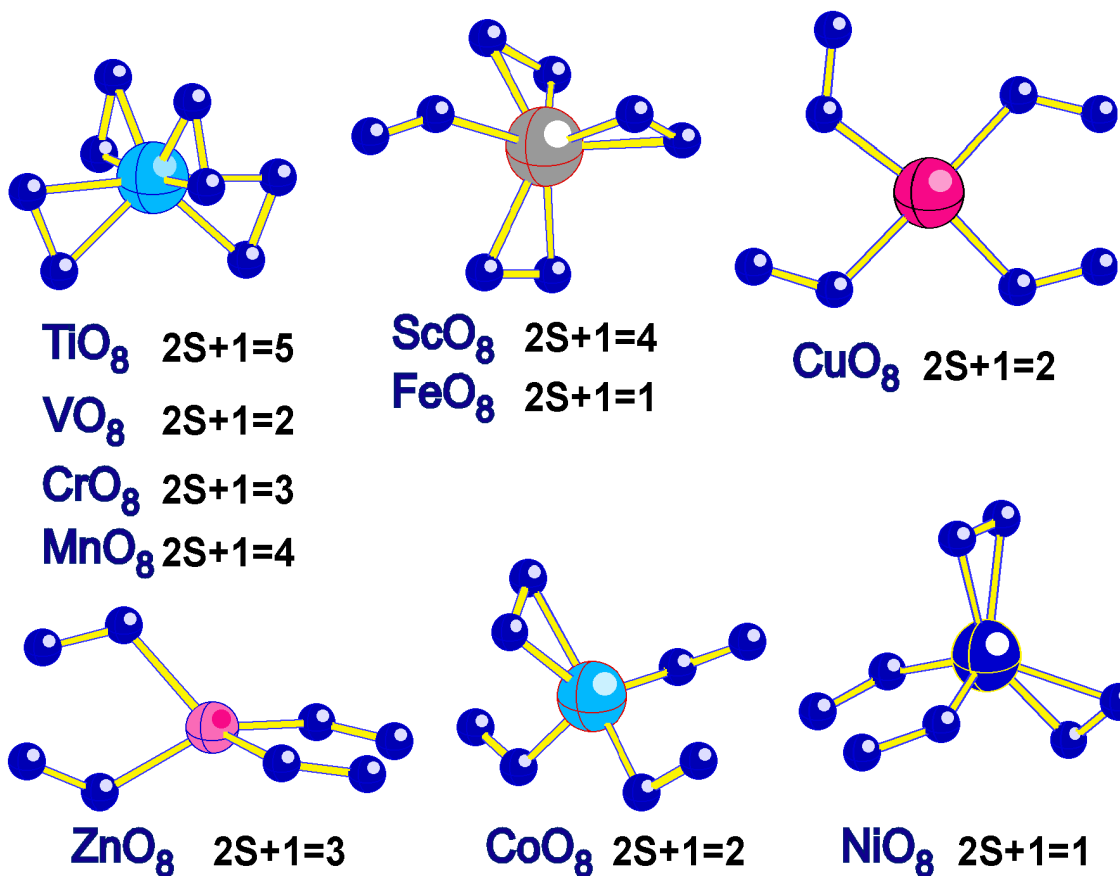
Summary

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=Sc-Zn)