DFT computational viewpoint of the Alpha oxygen – a unique oxidation active site

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Outline

This presentation describes the Alpha Oxygen (AO) which features an exceptional oxidation activity (CH_4 to CH_3OH at room temperature). The talk reveals that the structure of the AO was unknown when discovered, later suggested based only on DFT calculations, later derived from spectroscopic experiments and DFT and ab initio calculations.

Two new methods of the preparation of the AO were discovered on the basis of prior DFT calculations.

Zeolites

- Zeolites are crystalline microporous aluminosilicates widely used as molecular sieves and catalysts in industrial chemical processes.

- Transition metal exchanged zeolites – have exceptional redox catalytic properties: deNOx, selective oxidation of hydrocarbons by N_2O, N_2O decomposition, …

Alpha Oxygen (AO)

- Panov et al. (the Boreskov Institute of Catalysis in Novosibirsk) discovered the AO in the late 1980s.

- The AO attracted significant attention because of its exceptional oxidation activity.

- The AO features potential for applications:
  - oxidation of methane to methanol
  - oxidation of benzene to phenol
  - other selective oxidations.

Alpha Oxygen (AO)

- When discovered, the structure of the AO was unknown.

- Panov et al. defined the AO by its (i) exceptional oxidation capability (i.e., oxidation of CH_4 to CH_3OH at room temperature) and (ii) preparation method.

Preparation of the AO

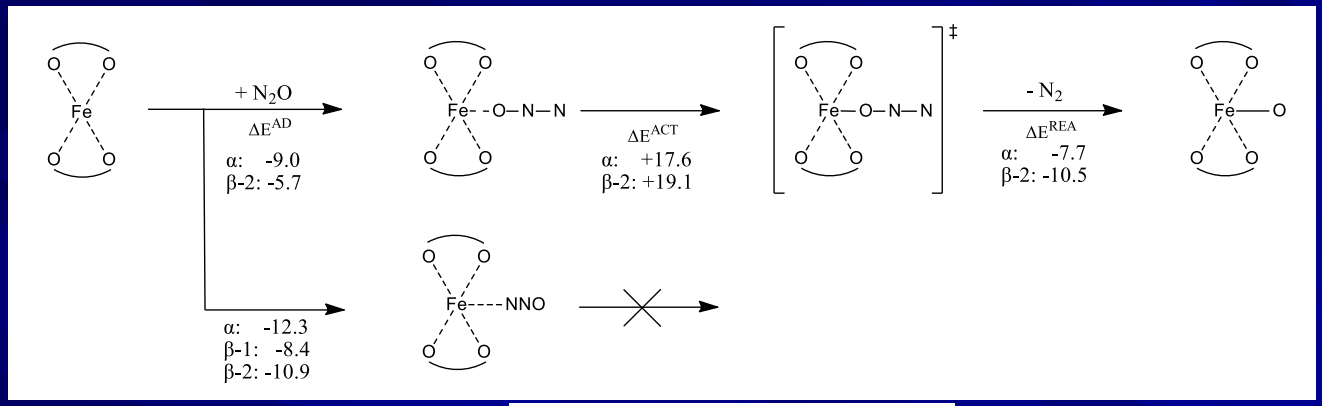
- 1st Zeolites containing Fe(II) oxidized by N_2O. The original method of Panov 1990.
- 2nd method 2020
- 3rd method 2026

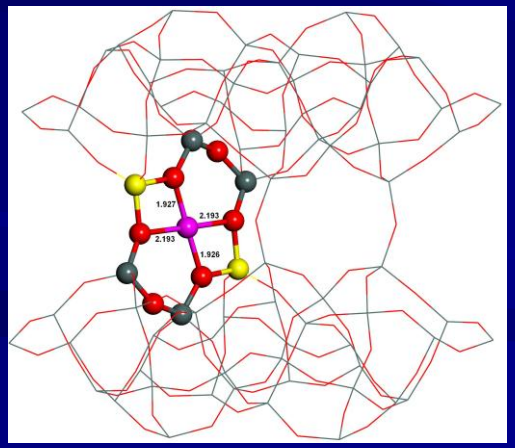
Structure (geometry) of the AO

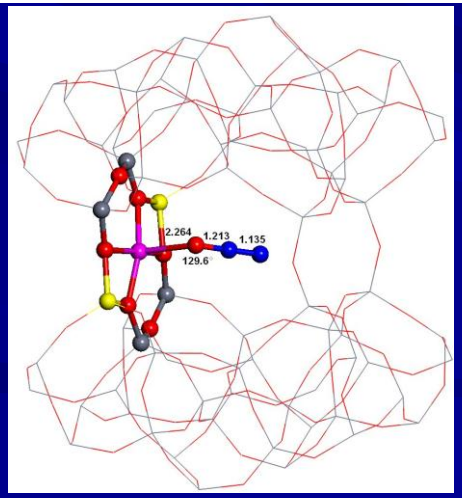
- The structure of the AO was suggested based on DFT calculations in the first decade of the new millennium by several groups **based on the preparation method**.
- No experimental support for the suggested structure at that time.
- Sklenak et al. were the first who used periodic DFT.

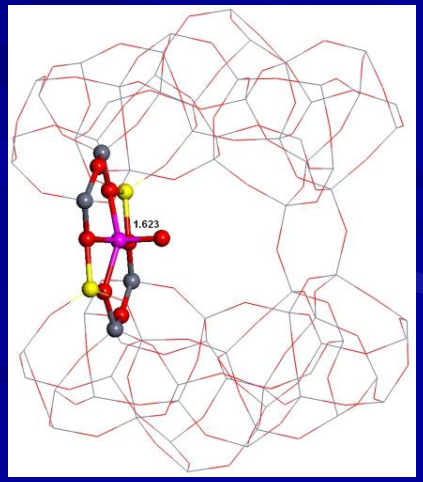
Structure (geometry) of the AO

Preparation of the AO: oxidation of Fe(II) in a zeolite matrix by N_2O (Panov 1990).





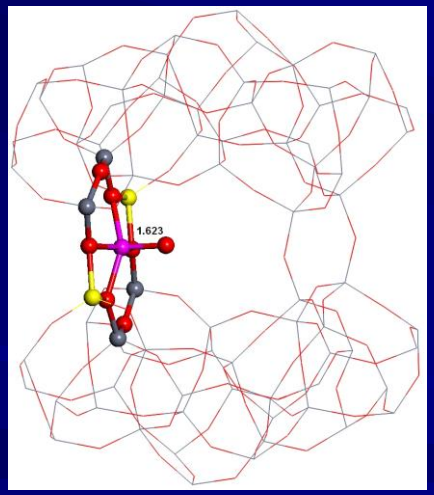




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Structure (geometry) of the AO

The structure of the Alpha oxygen in the Fe-beta zeolite was determined by Solomon and co-workers in 2016: Nature, 2016, 536, 317. However, they used circular dichroism spectroscopy + DFT and CASPT2 calculations.



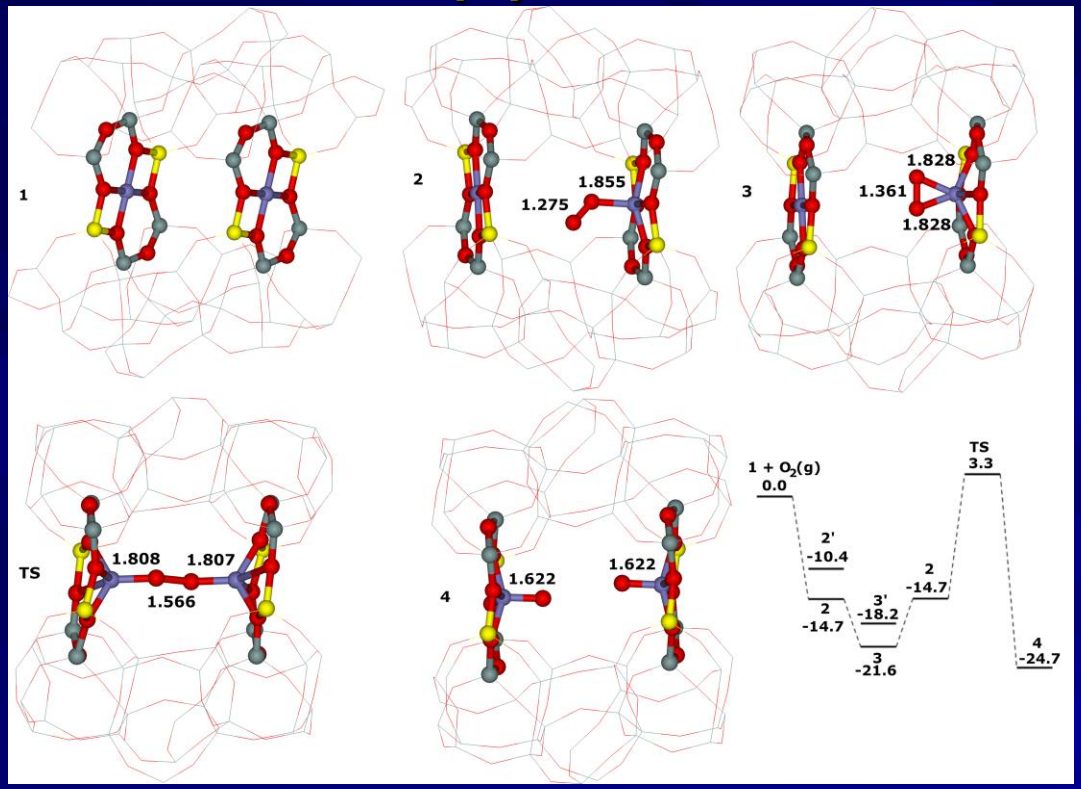
The structure of the AO determined by Solomon et al. was very close to our calculated structure in our prior paper: Sklenak S. et al. J. Catal. 2010, 272, 262.

No direct determination of the structure without DFT (no XRD, neutron or electron diffraction experiments) until now.

Preparation of the AO

- 1st Zeolites containing Fe(II) oxidized by N_2O. The original method of Panov 1990.
- 2nd Zeolite containing the distant binuclear Me(II) (Me = Fe, Co, Mn, and Ni) cationic sites oxidized by O_2 - Sklenak et al. 2020.
- 3rd method 2026

Formation of the AO from O_2 on distant binuclear Fe(II) cationic sites in ferrierite



The AO is able to selectively oxidize CH_4 at ROOM temperature

The first ever preparation of the AO on Fe(II) from O_2

economically beneficial, especially if air can be used

O_2 is by orders of magnitude cheaper than N_2O

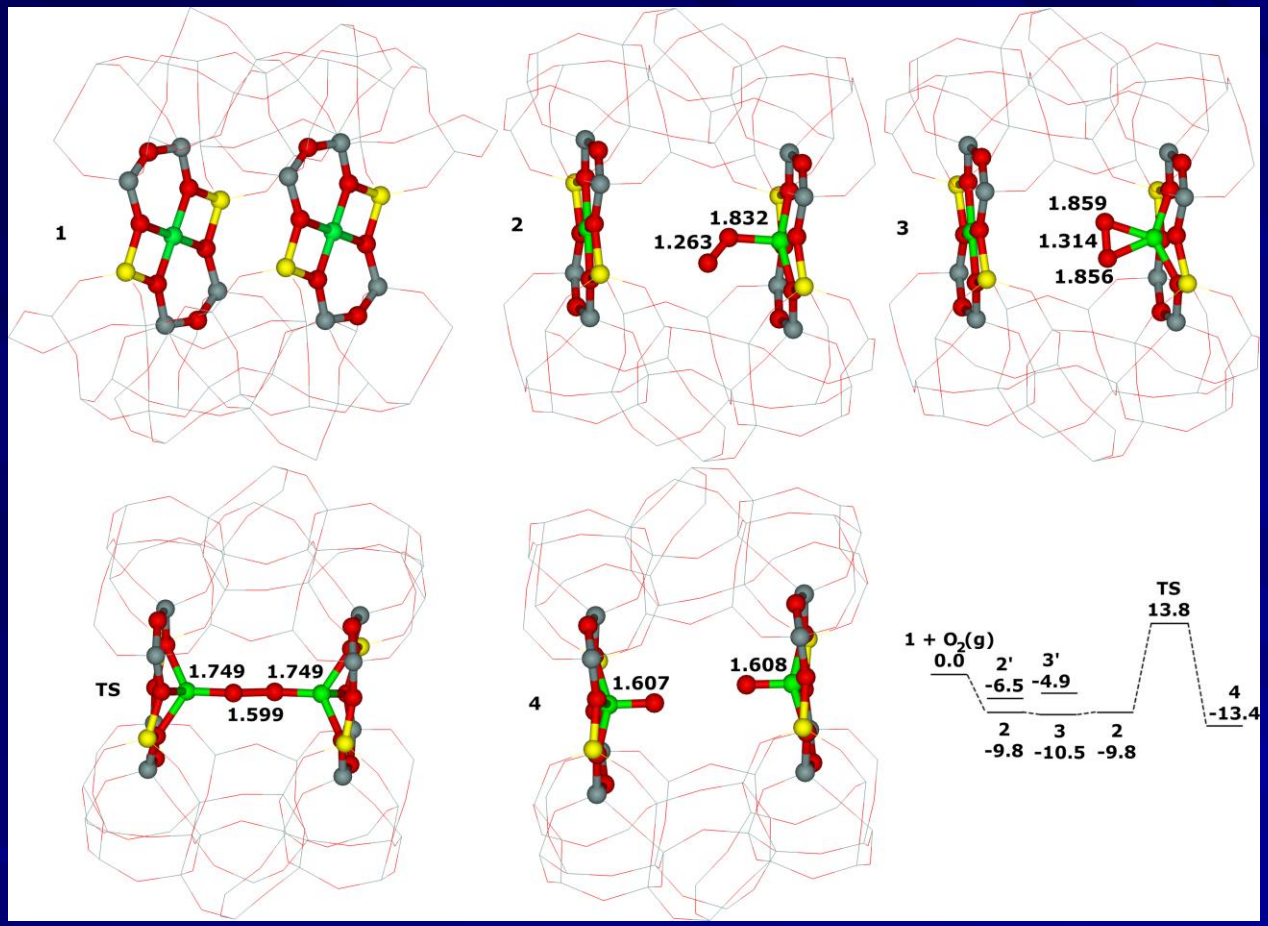
Tabor et al., Sci. Adv. 2020, 6:eaaz9776

This reaction had been FIRSTLY PREDICTED COMPUTATIONALLY before it was verified experimentally. This shows the enormous PREDICTIVE POWER of periodic DFT calculations.

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10th Users' Conference of IT4I,
November 5 -6, 2026, Ostrava

Formation of the AO from O_2 on distant binuclear Co(II) cationic sites in ferrierite



CALCULATIONS

Dedecek et al. Int. J. Quantum Chem. 2021, 121:e26611

EXPERIMENTS

Chem. Commun., 2021, 57, 3472

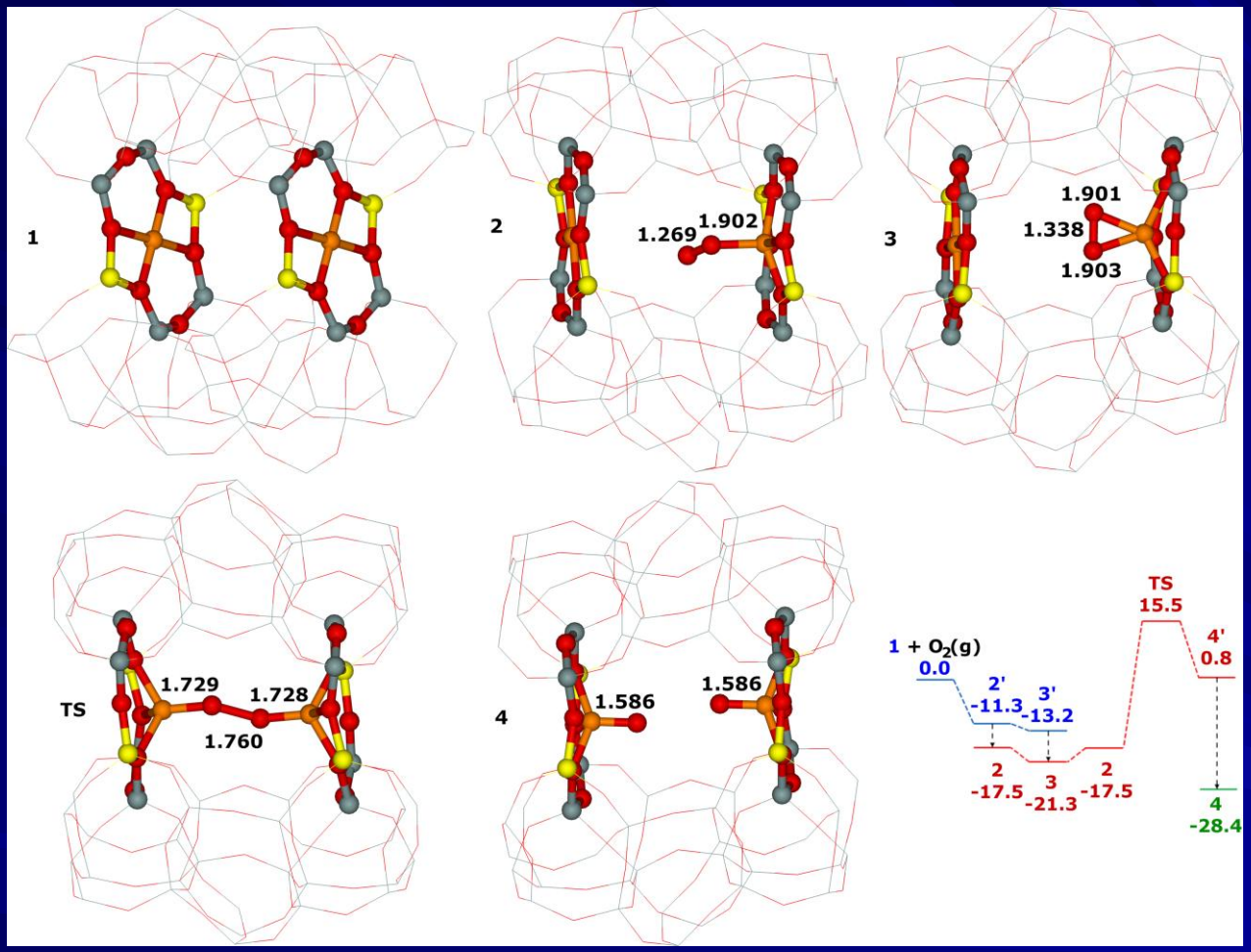
This reaction had been tested COMPUTATIONALLY before it was performed experimentally. This shows the POWER of periodic DFT calculations.

The first ever preparation of the Alpha oxygen on Co(II) from O_2.

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Formation of the AO from O_2 on distant binuclear Mn(II) cationic sites in ferrierite



CALCULATIONS

Dedecek et al. Int. J. Quantum Chem. 2021, 121:e26611

EXPERIMENTS

Chem. Commun., 2021, 57, 3472

This reaction had been tested COMPUTATIONALLY before it was performed experimentally. This shows the POWER of periodic DFT calculations.

The first ever preparation of the Alpha oxygen on Mn(II) from O_2.

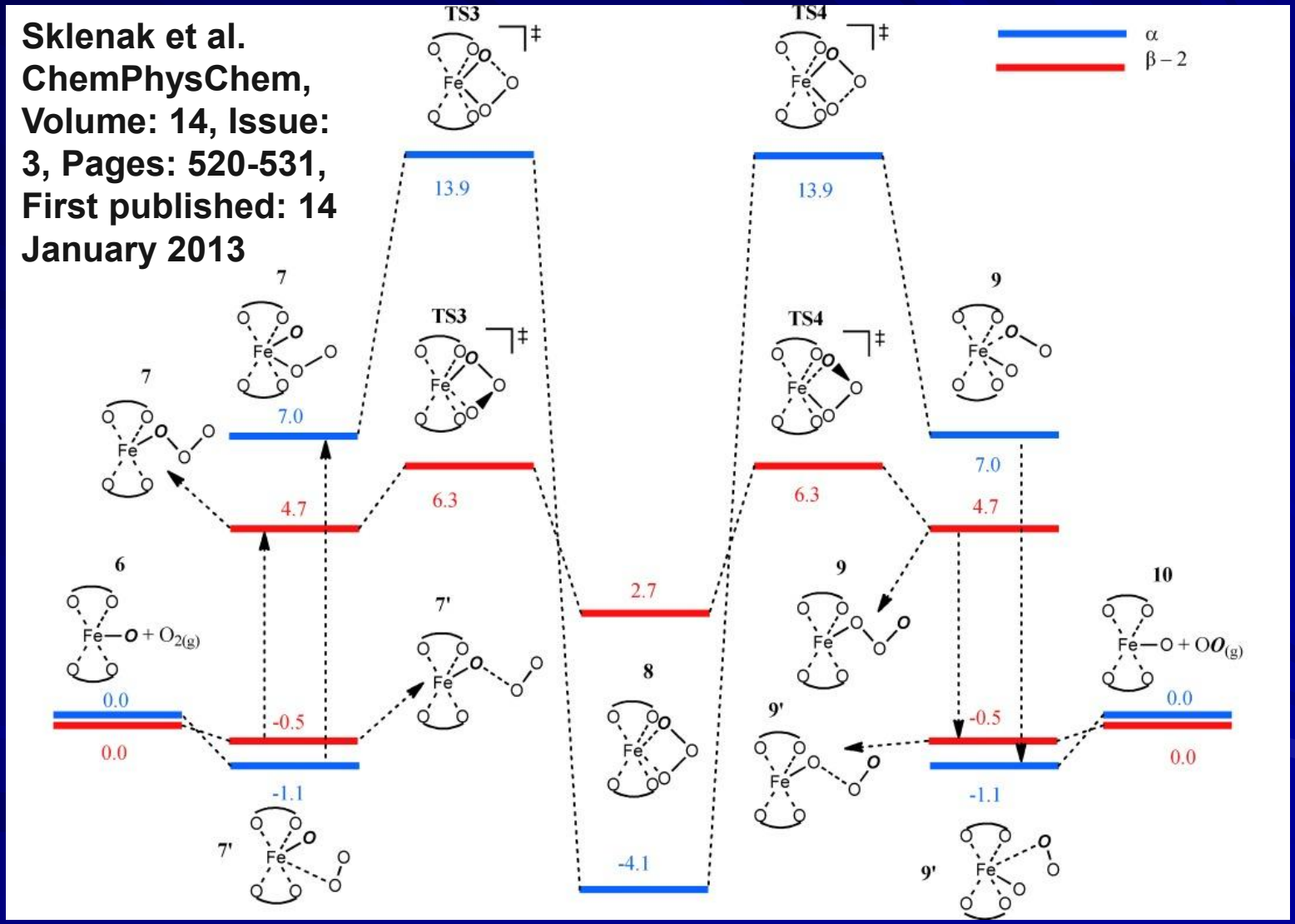
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Preparation of the AO

- 1st Zeolites containing Fe(II) oxidized by N_2O. The original method of Panov 1990.
- 2nd Zeolite containing the distant binuclear Me(II) (Me = Fe, Co, Mn, and Ni) cationic sites oxidized by O_2 - Sklenak et al. 2020.
- 3rd Zeolites containing Me(II) oxidized by O_3. The new method of Dedecek et al. 2026 is based on previous DFT calculations.

Preparation of the AO



Methods & Programs

- Molecular Dynamics (MD) and structure optimization (OPT):
  - Periodic-DFT (VASP program; Prof. Hafner of U Vienna)
    - Spin polarized Periodic-DFT calculations
    - PBE functional
    - Projector Augmented Wave method (PAW)
    - cutoff 600 eV for OPT
    - cutoff 400 eV for MD
    - Born Oppenheimer MD
    - NVT ensemble in MD

Conclusions

- The AO discovered by Panov et al. in the late 1980s features exceptional oxidation activity (CH_4 to CH_3OH at room temperature).
- The determination of the structure of the AO requires DFT/ab initio calculations. No diffraction experiments until now.

Conclusions

- Two new methods of the preparation of the AO were proposed based on prior DFT calculations
  - Oxidation of Me(II) of the distant binuclear cationic sites by O_2 – Sklenak et al. 2020
  - Oxidation of Me(II) by O_3 – Dedecek 2026.

- Study of oxidation reactions over the AO active sites – e.g., investigation of the oxidation of CH_4 to CH_3OH over pairs of the AO (2^{nd} method of preparation of the AO).

Acknowledgments

- Res. Prof. Jiri Dedecek
- The supercomputer center in Ostrava