Atomistic insights into surface oxidation of pyrite and quartz: implications for ultrafine particle toxicity

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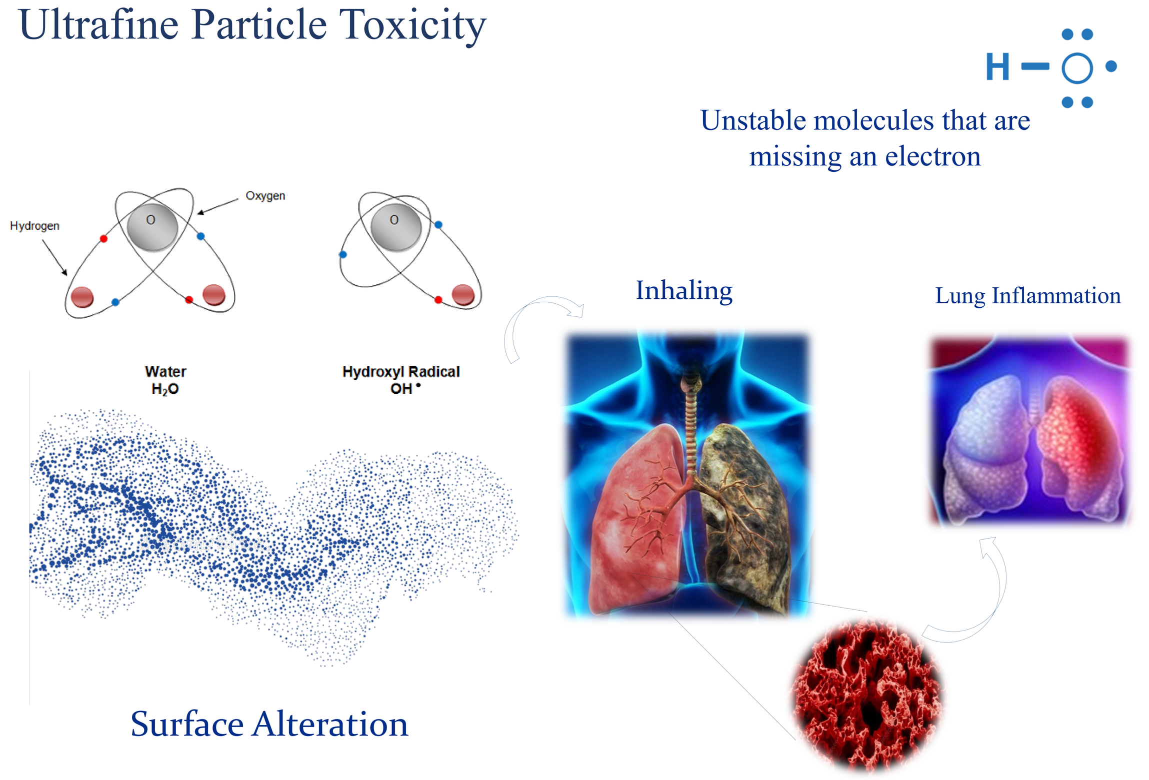
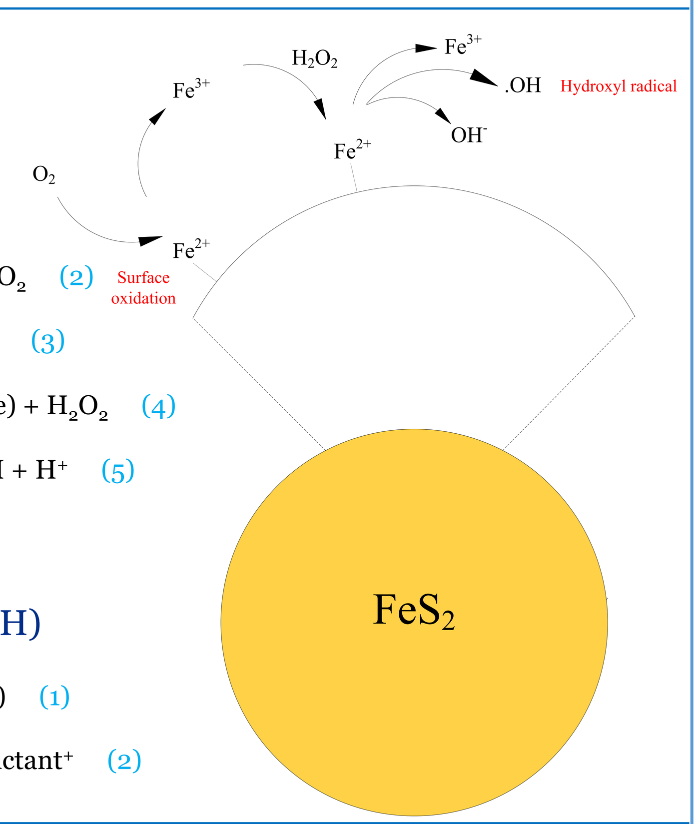
Background

Ultrafine Particle Toxicity



Pyrite surface



$Fe^{II}(aq) + O_2 \rightarrow Fe^{III}(aq) + (O_2^{\bullet})^-$ (1)

$Fe^{II}(aq) + (O_2^{\bullet})^- + 2H^+ \rightarrow Fe^{III}(aq) + H_2O_2$ (2)

$Fe^{II}(pyrite) + O_2 \rightarrow Fe^{III}(pyrite) + (O_2^{\bullet})^-$ (3)

$Fe^{II}(pyrite) + (O_2^{\bullet})^- + 2H^+ \rightarrow Fe^{III}(pyrite) + H_2O_2$ (4)

$Fe^{III}(pyrite) + H_2O \rightarrow Fe^{II}(pyrite) + {}^{\bullet}OH + H^+$ (5)

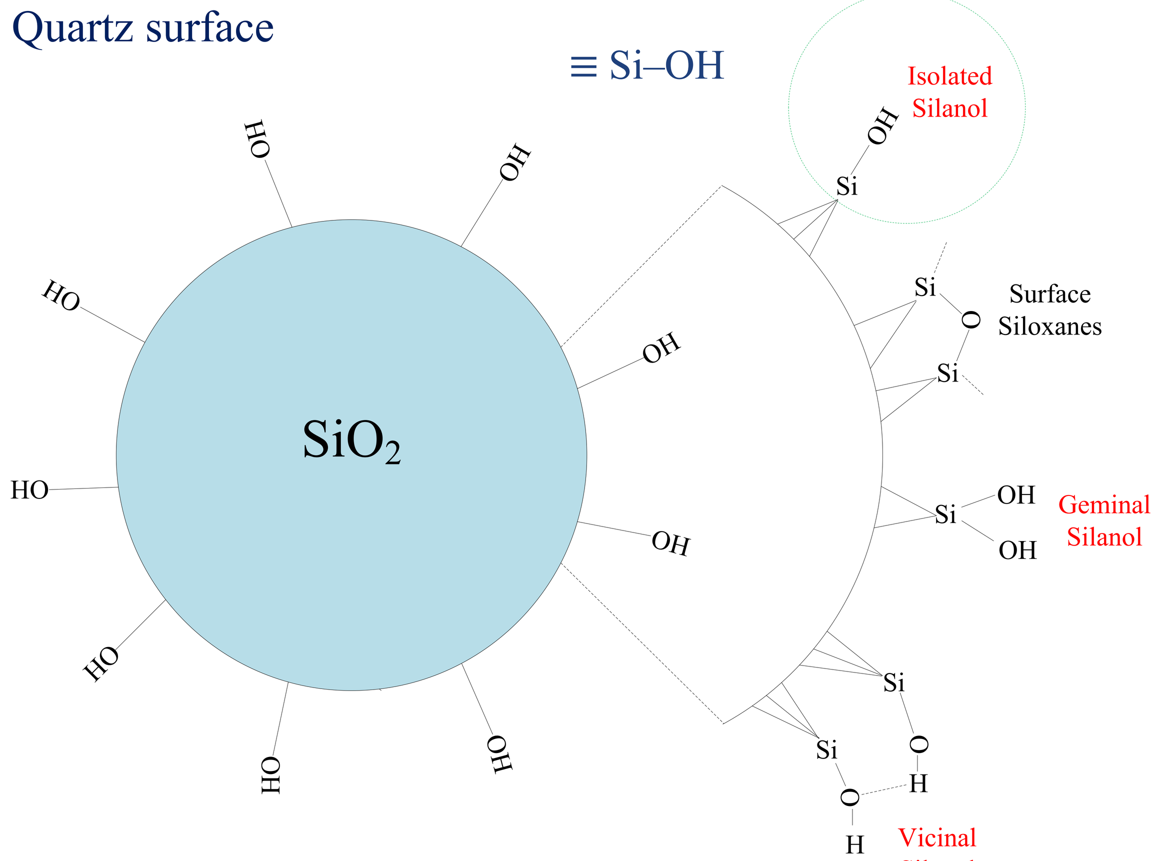
$2{}^{\bullet}OH \rightarrow H_2O_2$ (6)

Fenton Reaction ($H_2O_2 \rightarrow {}^{\bullet}OH$)

$Fe^{II}(aq) + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- + Fe^{III}(aq)$ (1)

$Fe^{III}(aq) + Reductant \rightarrow Fe^{II}(aq) + Reductant^+$ (2)

Quartz surface



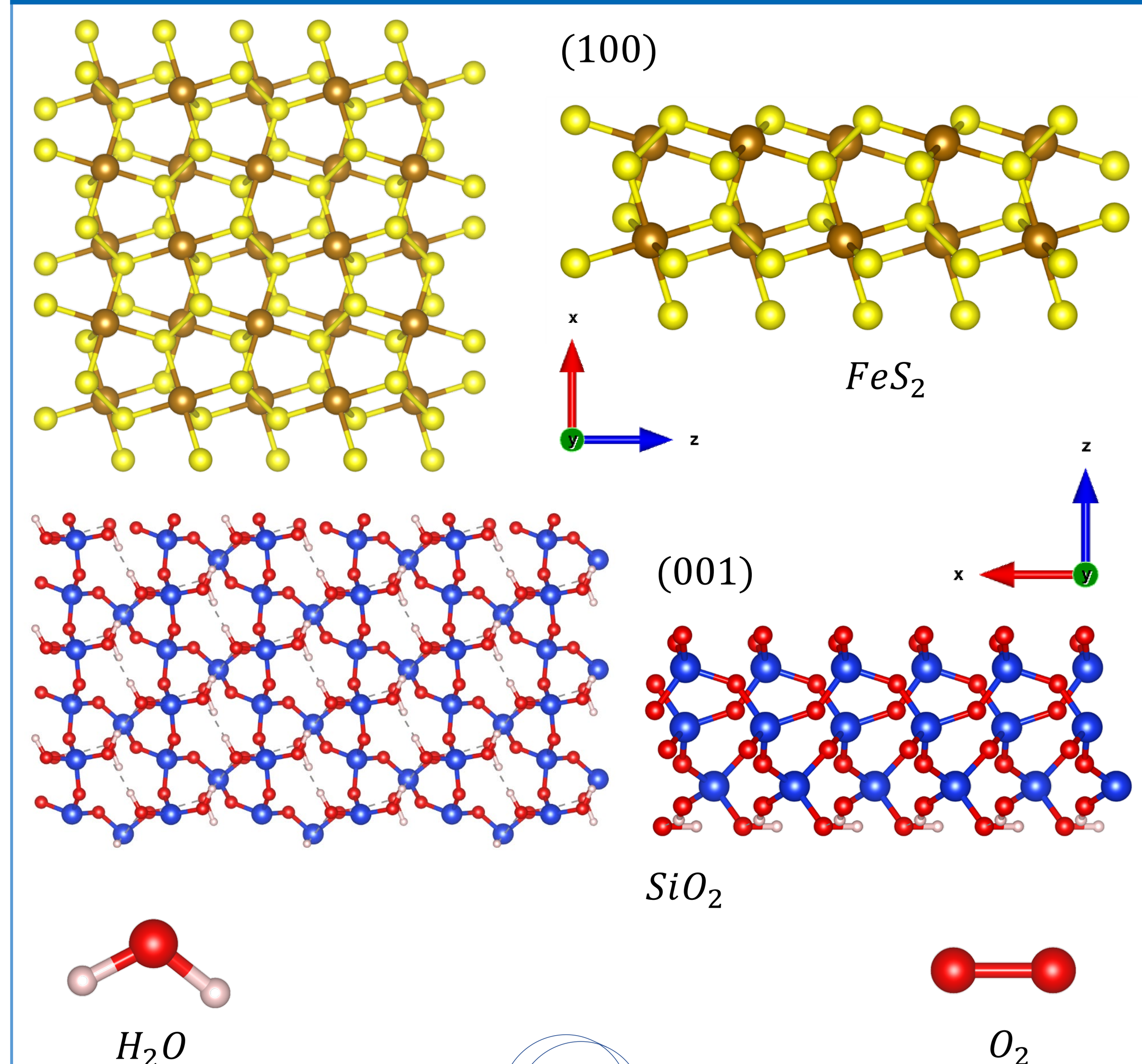
$\equiv SiO\cdot + H_2O \rightarrow \equiv SiOH + \cdot OH$

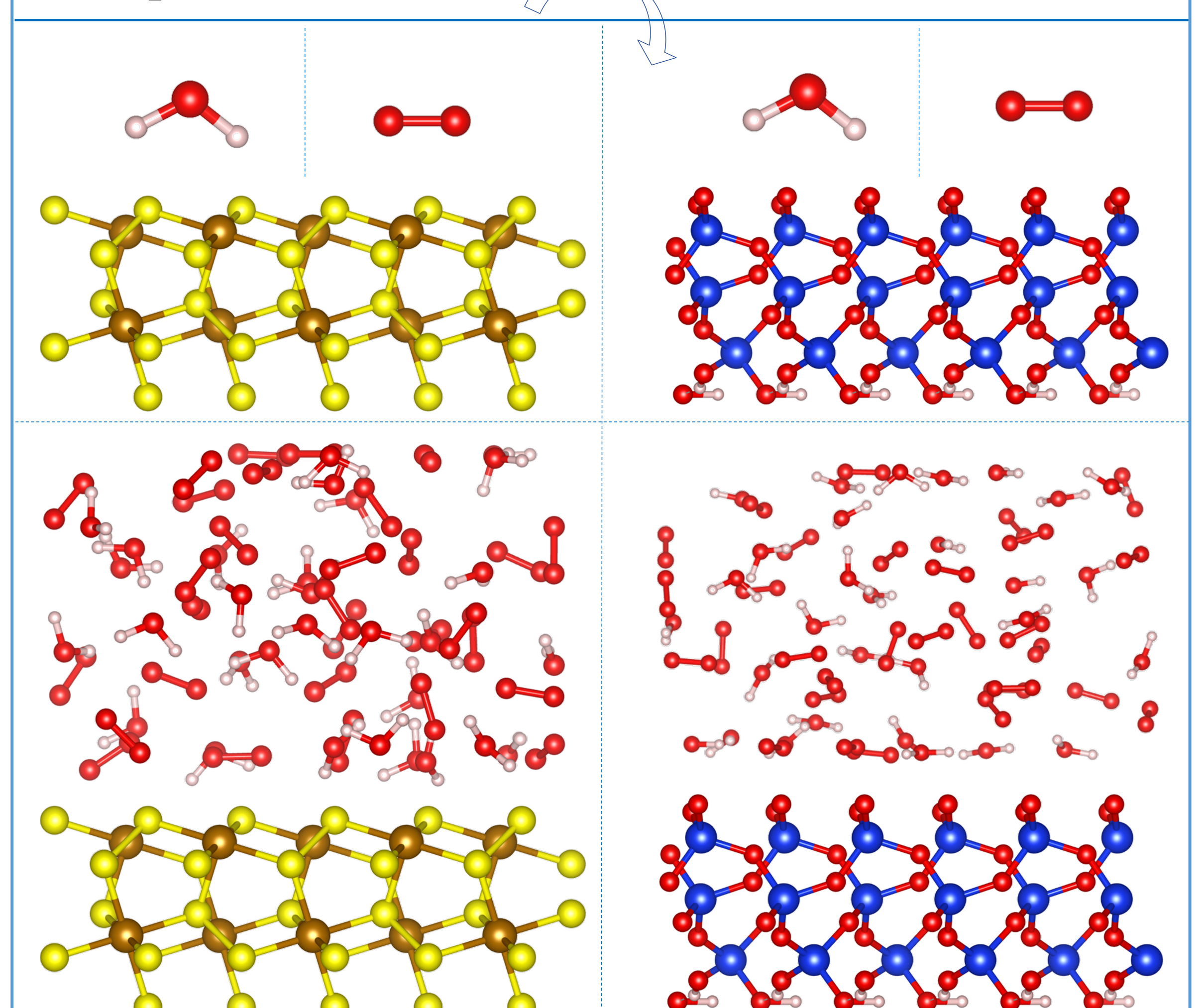
$\equiv SiO\cdot + \cdot OH \rightarrow \equiv SiOOH$

$\equiv SiOOH + H_2O \rightarrow \equiv SiO\cdot + H_2O_2$

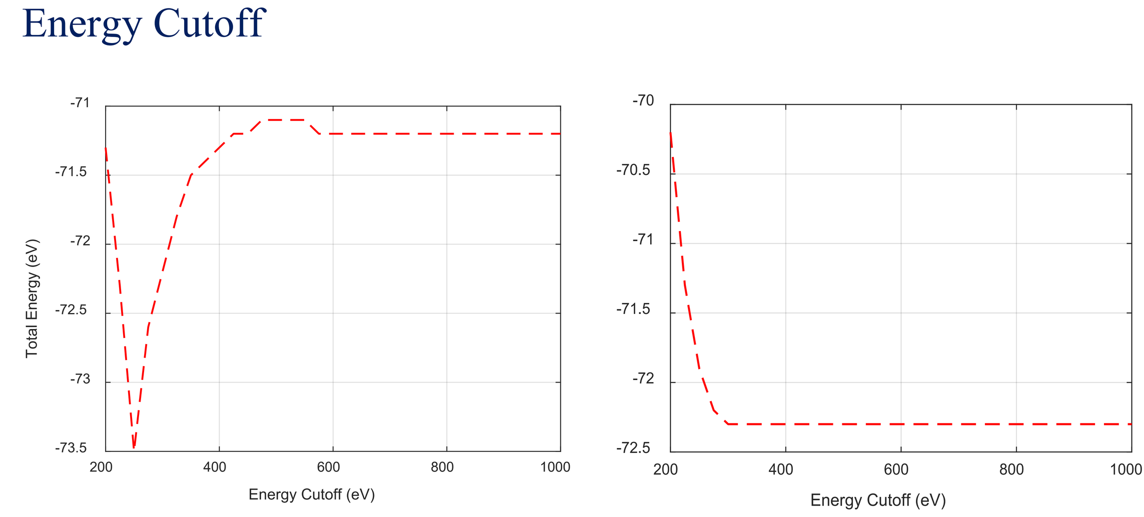
Surface oxidation of pyrite and quartz, as the two main dust composing minerals, were studied using quantum mechanical simulations. Such insights are important because the formation of free radicals as a result of particle surface alteration brings about the bioactivity of ultrafine particles.

Materials and Methods





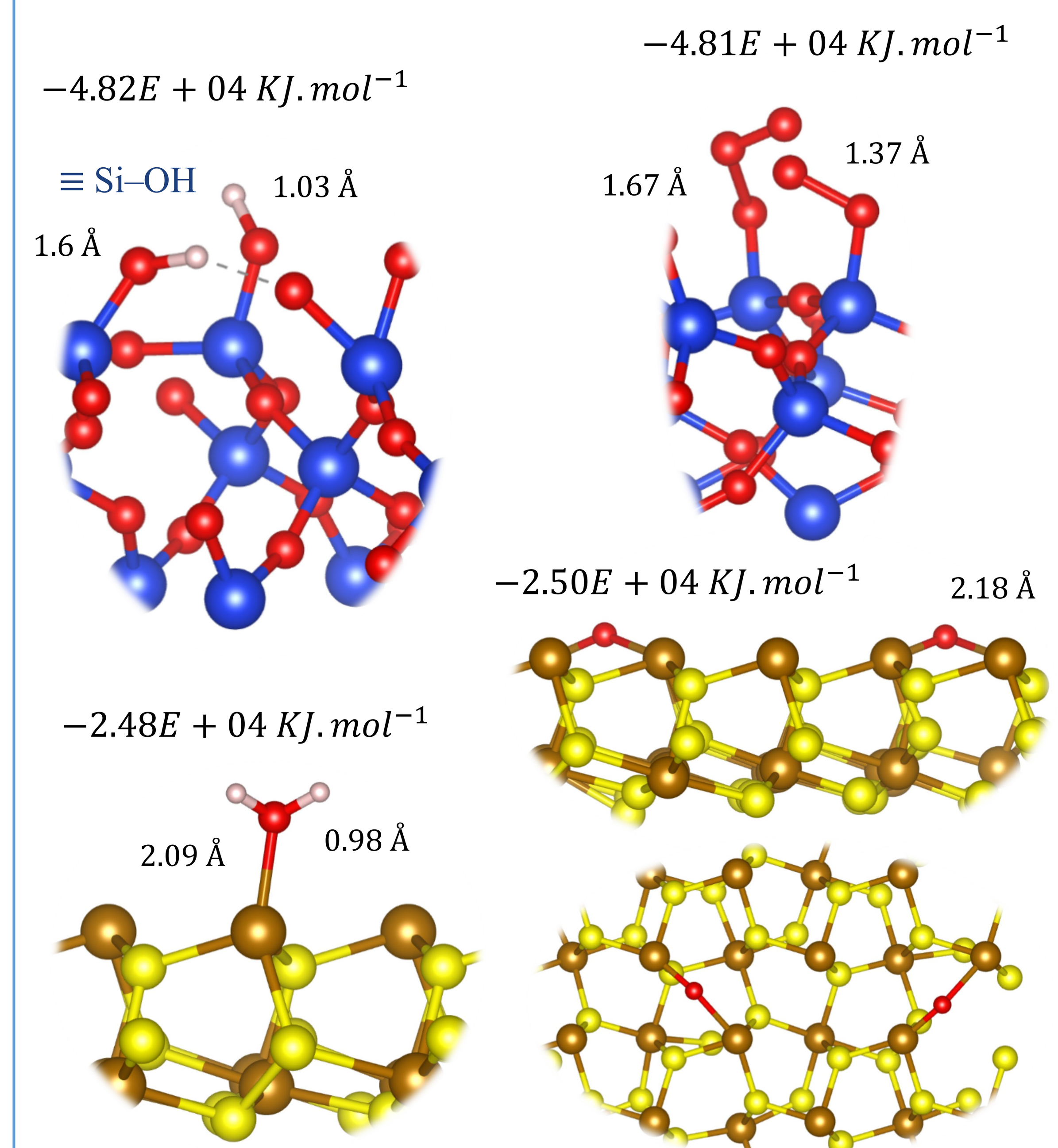
Energy Cutoff

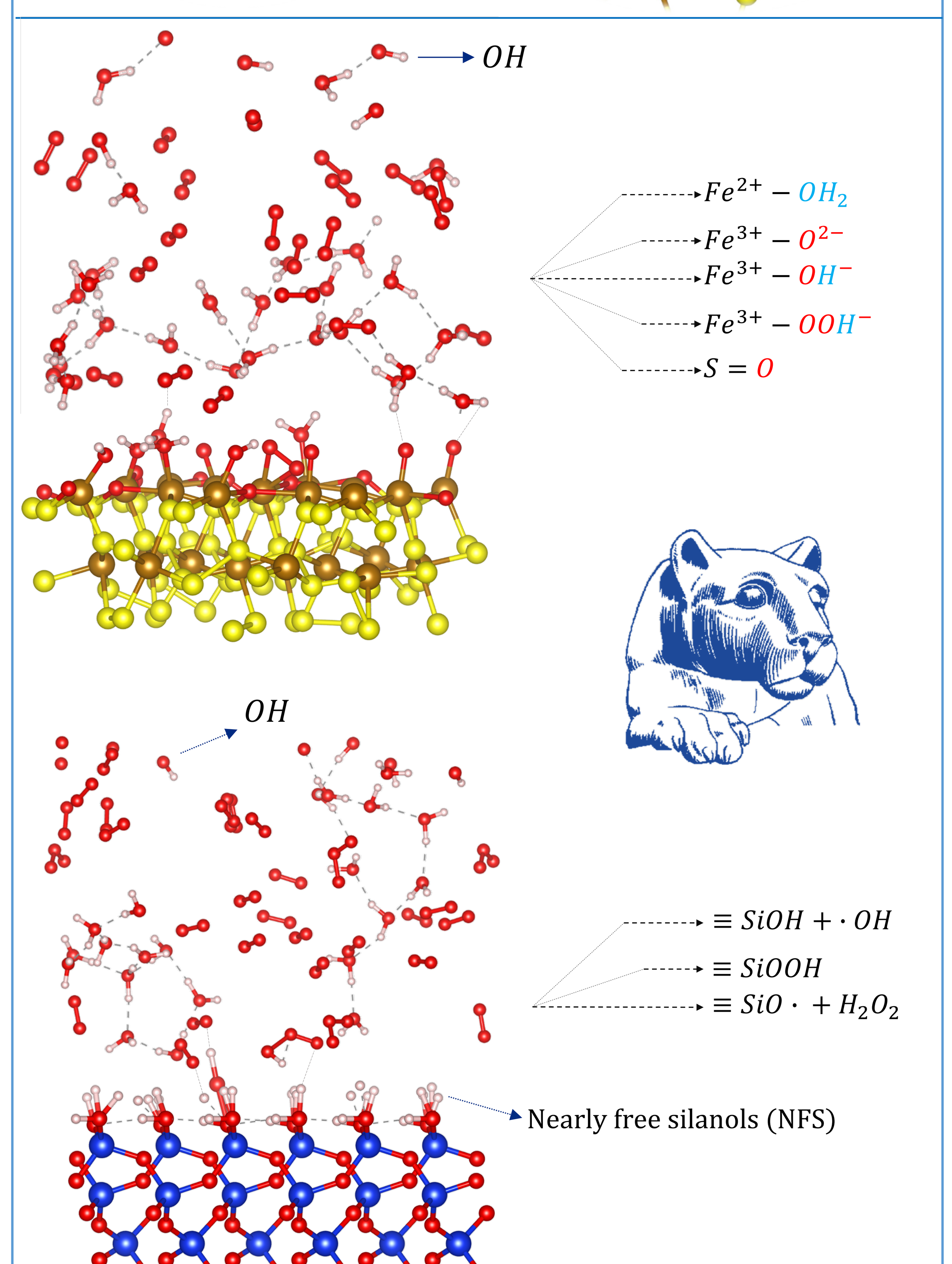


Vienna Ab-initio Simulation Package (VASP) · python

Results

Adsorption of single molecules





Conclusions

- Adsorption of H_2O molecule on the surface of quartz is slightly more thermodynamically favorable than O_2;
- Such interactions entail the formation of $\equiv SiOH$, $\cdot OH$ radicals, and peroxyl defects;
- On the surface of pyrite, the adsorption of O_2 is more thermodynamically favorable than H_2O;
- Pyrite surface oxidation is due mainly to the presence of O_2 molecules;
- Such interactions lead to the formation of $Fe^{2+}-OH_2$, $Fe^{3+}-O^{2-}$, $Fe^{3+}-OH^-$, $Fe^{3+}-OOH^-$, $S=O$, and $\cdot OH$ radicals.

References

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Acknowledgments

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