

Revision 1

Supplemental material for

Interfacial structures and acidity constants of goethite from first principles molecular
dynamics simulations

YINGCHUN ZHANG,[†] XIANDONG LIU,^{*,†} JUN CHENG,[‡] XIANCAI LU[†]

[†]State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and
Engineering, Nanjing University, Nanjing, Jiangsu 210023, P. R. China

[‡]College of Chemistry and Chemical Engineering, Xiamen University, Xiamen,
Fujian 361005, P. R. China

*Corresponding author: xiandongliu@gmail.com. Tel: +86 25 83594664, Fax: +86 25
83686016.

Number of pages: 11

Number of tables: 2

Number of figures: 2

This file includes the following contents:

S1. Density profiles of water

FIGURE S1. Water density profiles

S2. Additional information for pKa calculation

S2.1 pKa calculation method

Table S1. The parameters used in restraining the dummy atoms

FIGURE S2. Vertical energy gaps of (110) $\equiv\text{Fe}_3\text{O}_\text{U}\text{H}$ and (021) $\equiv\text{Fe}_2\text{OH}_2$

Table S2. Calculated vertical energy gaps, thermodynamic integrals, and pKa values

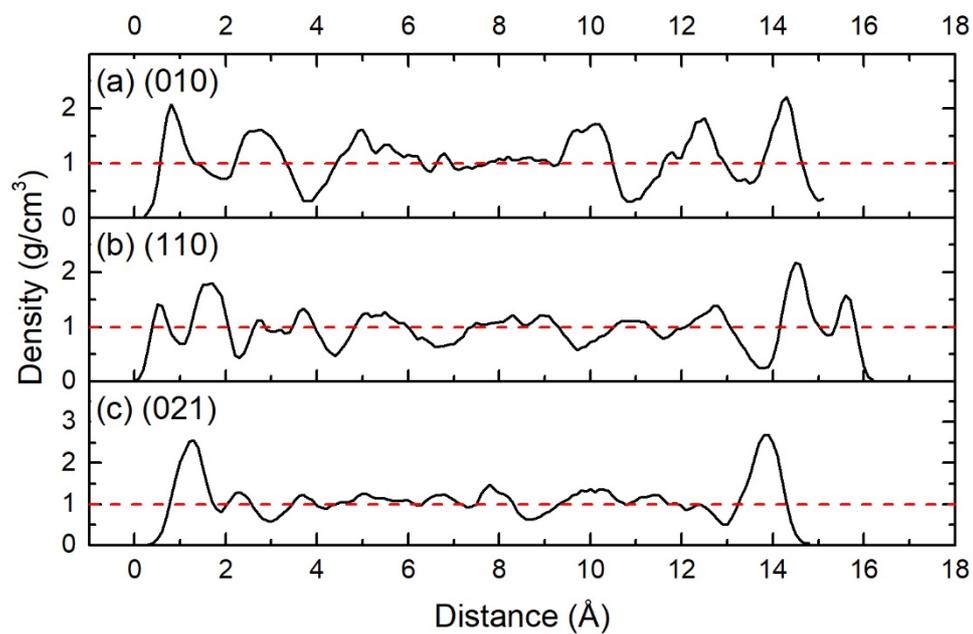
S1. Density profiles of water

FIGURE S1. Water density profiles of (a) (010), (b) (110) and (c) (021) systems. The mid-plane between surface O atoms and water O atoms was taken as the starting point of the profile for each system.

S2. Additional information for pKa calculation

S2.1 pKa calculation method

The pKa values of goethite surface groups were evaluated via the half-reaction scheme of the vertical energy gap method (Sulpizi and Sprik, 2008; Cheng et al., 2009; Costanzo et al., 2011; Cheng and Sprik, 2012). With this scheme, the proton of the acid site (labeled as AH) is gradually transformed into a classical particle with no charge (i.e. the dummy atom). The free energy change associated with this process is calculated with the thermodynamic integration relation:

$$\Delta_{dp}A_{AH} = \int_0^1 d\eta \langle \Delta_{dp}E_{AH} \rangle_{r\eta} \quad (1)$$

η is the coupling parameter that increased from 0 (reactant) to 1 (product). $\Delta_{dp}E$ is the vertical energy gap, which is defined as the potential energy difference between the reactant and product state. This value is obtained from the MD trajectory produced by sampling the restrained mapping Hamiltonian:

$$H_\eta = (1-\eta)H_R + \eta H_P + V_r \quad (2)$$

Here H_R and H_P stand for the reactant and product state respectively. The harmonic restraint (V_r) is applied on the dummy atom to keep it in the location resembling the reactant state:

$$V_r = \sum_{bonds} \frac{1}{2} k_d (d - d_0)^2 + \sum_{angles} \frac{1}{2} k_\theta (\theta - \theta_0)^2 \quad (3)$$

This harmonic potential consists of the bond stretching and angle bending terms whose equilibrium values are d_0 and θ_0 , respectively. The equilibrium values used for each surface group were derived from the simulations without restraints and the force constants k_d and k_θ were selected according to previous studies (Sulpizi and Sprik, 2008; Cheng et al., 2009). The parameters of V_r are given in Table S1. The 3-point Simpson's rule (Eq. 4) was employed to evaluate the integral in Eq. 1 for most of the surface groups. For $\equiv\text{Fe}_3\text{O}_\text{UH}$ on (110) surface and $\equiv\text{Fe}_2\text{OH}$ on (021) surface, the 5-point formula (Eq. 5) was used due to the significant nonlinearities of ΔE in these two systems.

$$\Delta_{dp}A_{AH} = \frac{1}{6}(\langle\Delta E\rangle_0 + \langle\Delta E\rangle_1) + \frac{2}{3}\langle\Delta E\rangle_{0.5} \quad (4)$$

$$\Delta_{dp}A_{AH} = \frac{1}{12}(\langle\Delta E\rangle_0 + \langle\Delta E\rangle_1 + 4(\langle\Delta E\rangle_{0.25} + \langle\Delta E\rangle_{0.75}) + 2\langle\Delta E\rangle_{0.5}) \quad (5)$$

With the same procedure, one proton of a hydronium located in the solution region is transformed into a dummy atom, and the associated free energy is calculated with Eq. 1. The final pKa is calculated according to the formula:

$$2.3k_B T pK_a = \int_0^1 d\eta \langle \Delta_{dp} E_{AH} \rangle_{r\eta} - \int_0^1 d\eta \langle \Delta_{dp} E_{H_3O^+} \rangle_{r\eta} + k_B T \ln [c^0 \Lambda_{H^+}^3] \quad (6)$$

$c^0 = 1 \text{ mol/L}$ is the unit molar concentration and $\Lambda_{H^+}^3$ means the thermal wavelength of the proton (Costanzo et al., 2011). The last term stands for the translational entropy generated by the acid dissociation and can be approximated by the chemical potential of a free proton at the standard concentration, which equals to -0.19 eV.

The convergence of the pKa calculation was determined by monitoring the vertical energy gap. By taking $\equiv\text{Fe}_3\text{O}_\text{U}\text{H}$ on (110) surface and $\equiv\text{Fe}_2\text{OH}_2$ on (021) surface as examples, Figure S2 shows the raw vertical energy gap data and the accumulative averages, where one can see that the vertical energy gaps were all converged within 0.19 eV in the periods. This is consistent with the observation in our previous calculations that ΔE converged on a typical FPMD timescale e.g., (Cheng et al., 2009; Liu et al., 2013; Cheng et al., 2014)

Table S1. The parameters used in restraining the dummy atoms (harmonic potentials in Eq. (3)). H_d represents the dummy atom. n_d and n_θ mean the number of restrained bonds and angles, respectively. d_0 stands for equilibrium bond lengths (in Bohr), and θ_0 stands for equilibrium angles (in radian).

Surface	Group	n_d	d_0	k_d	n_θ	θ_0	k_θ
(010)	$\equiv\text{FeOH}_2$	1	1.87	1.0	2	1.92 (Fe-O- H_d)	0.1
						1.83 (H-O- H_d)	0.1
	$\equiv\text{Fe}_2\text{OH}$	1	1.87	1.0	2	1.86 (Fe-O- H_d)	0.1
						1.86 (Fe-O- H_d)	0.1
	$\equiv\text{Fe}_2\text{OH}_2$	2	1.87	1.0	3	1.86 (Fe-O- H_d)	0.1
						1.86 (Fe-O- H_d)	0.1
						1.94 (H-O- H_d)	0.1
	H_3O^+	3	1.89	1.0	2	1.94 (H-O- H_d)	0.1
						1.89 (H-O- H_d)	0.1
						1.89 (H-O- H_d)	0.1
(110)	$\equiv\text{FeOH}$	1	1.87	1.0	1	1.95 (Fe-O- H_d)	0.1
	$\equiv\text{FeOH}_2$	2	1.89	1.0	2	1.90 (H-O- H_d)	0.1
						2.09 (Fe-O- H_d)	0.1
	$\equiv\text{Fe}_2\text{OH}$	1	1.87	1.0	2	1.97 (Fe-O- H_d)	0.1
						1.97 (Fe-O- H_d)	0.1
	$\equiv\text{Fe}_2\text{OH}_2$	2	1.89	1.0	3	2.01 (Fe-O- H_d)	0.1
						2.01 (Fe-O- H_d)	0.1
						1.88 (H-O- H_d)	0.1
	$\equiv\text{Fe}_3\text{O}_L\text{H}$	1	1.87	1.0	3	2.23 (Fe-O- H_d)	0.1
						1.94 (Fe-O- H_d)	0.1
						1.94 (Fe-O- H_d)	0.1
	$\equiv\text{Fe}_3\text{O}_U\text{H}$	1	1.87	1.0	3	2.09 (Fe-O- H_d)	0.1
						2.09 (Fe-O- H_d)	0.1
						1.99 (Fe-O- H_d)	0.1
	$\equiv\text{Fe}_3\text{OH}$	1	1.87	1.0	3	1.84 (Fe-O- H_d)	0.1
1.84 (Fe-O- H_d)						0.1	
1.84 (Fe-O- H_d)						0.1	

	H ₃ O ⁺	3	1.89	1.0	2	1.94 (H-O-H _d)	0.1
			1.89	1.0		1.94 (H-O-H _d)	0.1
			1.89	1.0			
(021)	≡FeO _h H ₂	1	1.89	1.0	2	1.83 (Fe-O-H _d)	0.1
						1.86 (H-O-H _d)	0.1
	≡FeOH	1	1.85	1.0	1	2.08 (Fe-O-H _d)	0.1
	≡FeOH ₂	1	1.89	1.0	2	1.93 (Fe-O-H _d)	0.1
						1.83 (H-O-H _d)	0.1
	≡Fe ₂ OH	1	1.89	1.0	2	1.88 (Fe-O-H _d)	0.1
						1.88 (Fe-O-H _d)	0.1
	≡Fe ₂ OH ₂	2	1.89	1.0	3	1.84 (Fe-O-H _d)	0.1
			1.89	1.0		1.84 (Fe-O-H _d)	0.1
						1.96 (H-O-H _d)	0.1
	≡Fe ₂ O _h H	1	1.89	1.0	2	2.02 (Fe-O-H _d)	0.1
						2.02 (Fe-O-H _d)	0.1
	≡Fe ₂ O _h H ₂	2	1.89	1.0	3	1.81 (Fe-O-H _d)	0.1
			1.89	1.0		1.81 (Fe-O-H _d)	0.1
						1.83 (H-O-H _d)	0.1
	H ₃ O ⁺	3	1.89	1.0	2	1.94 (H-O-H _d)	0.1
			1.89	1.0		1.94 (H-O-H _d)	0.1
			1.89	1.0			

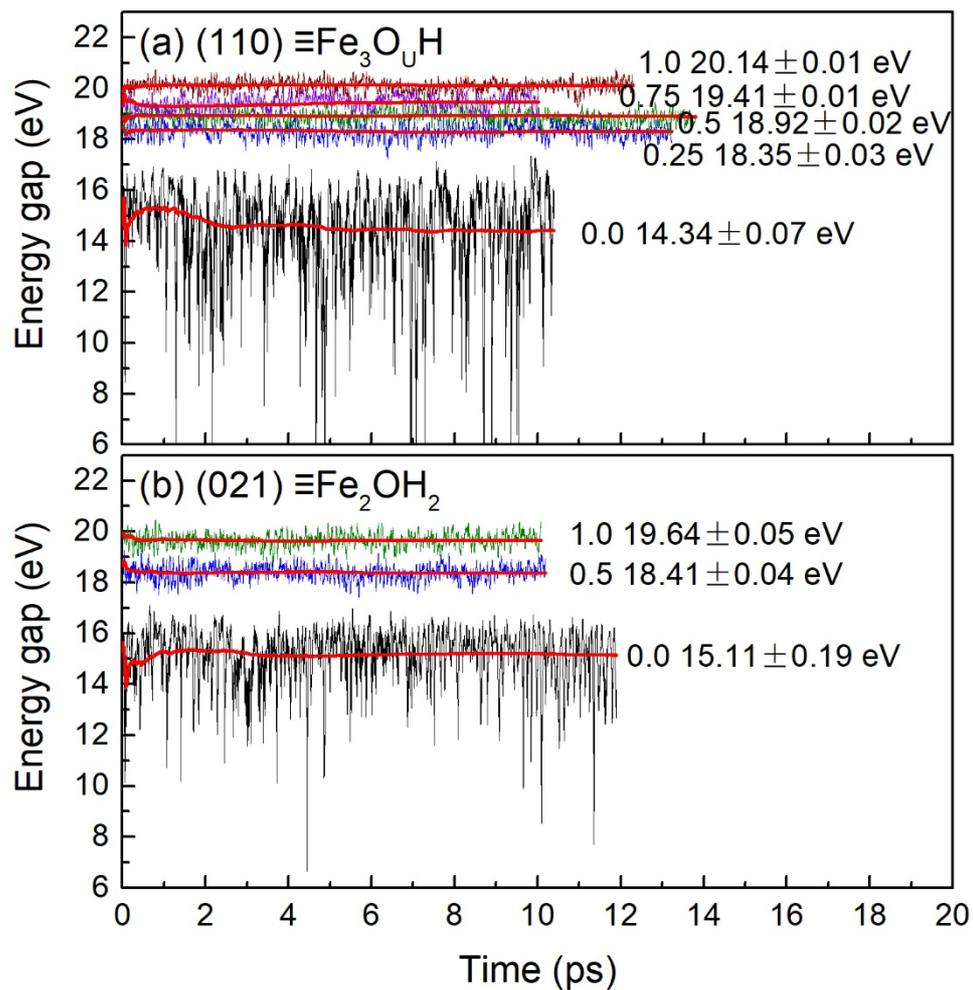


FIGURE S2. The accumulative averages of vertical energy gaps for (a) $\equiv \text{Fe}_3\text{O}_u\text{H}$ on (110) surface and (b) $\equiv \text{Fe}_2\text{OH}_2$ on (021) surface. The statistical error was estimated as the difference between the first and the second half of the production run.

Table S2. Calculated vertical energy gaps (in eV), thermodynamic integrals (in eV), and pKa values.

Surface	Group	$\eta=0.0$	$\eta=0.25$	$\eta=0.5$	$\eta=0.75$	$\eta=1.0$	ΔA	pKa
(010)	$\equiv\text{FeOH}_2$	14.85±0.06		19.90±0.08		21.21±0.08	19.28±0.08	10.9±1.8
	$\equiv\text{Fe}_2\text{OH}$	17.81±0.01		19.69±0.01		20.72±0.04	19.55±0.01	15.4±0.7
	$\equiv\text{Fe}_2\text{OH}_2$	17.41±0.01		18.91±0.03		20.40±0.02	18.91±0.02	4.7±0.8
	H_3O^+	14.04±0.01		19.00±0.03		20.58±0.07	18.44±0.03	
(110)	$\equiv\text{FeOH}_2$	15.85±0.02		18.75±0.01		19.97±0.03	18.47±0.01	7.3±0.5
	$\equiv\text{FeOH}$	16.64±0.11		19.20±0.01		20.14±0.01	18.93±0.02	15.0±0.7
	$\equiv\text{Fe}_2\text{OH}$	17.98±0.04		18.82±0.01		19.93±0.02	18.86±0.02	13.9±0.7
	$\equiv\text{Fe}_2\text{OH}_2$	14.62±0.19		18.39±0.03		19.84±0.05	18.00±0.06	-0.5±1.3
	$\equiv\text{Fe}_3\text{O}_L\text{H}$	15.80±0.05		19.04±0.01		20.08±0.01	18.67±0.01	10.7±0.5
	$\equiv\text{Fe}_3\text{O}_U\text{H}$	14.34±0.07	18.35±0.03	18.92±0.02	19.41±0.01	20.14±0.01	18.61±0.02	9.7±0.7
	$\equiv\text{Fe}_3\text{O}$	16.95±0.01		17.98±0.04		19.41±0.04	18.05±0.03	0.3±0.8
	H_3O^+	14.36±0.01		18.17±0.02		19.99±0.01	17.84±0.02	
(021)	$\equiv\text{FeO}_h\text{H}_2$	15.75±0.20		19.05±0.01		20.46±0.01	18.74±0.04	10.0±1.5
	$\equiv\text{FeOH}$	16.50±0.08		19.12±0.05		20.23±0.10	18.87±0.05	12.2±1.7
	$\equiv\text{FeOH}_2$	14.99±0.02		18.62±0.01		20.22±0.07	18.28±0.02	2.3±1.2
	$\equiv\text{Fe}_2\text{OH}$	15.64±0.04	17.64±0.05	18.67±0.01	19.46±0.04	19.97±0.01	18.45±0.03	5.2±1.3
	$\equiv\text{Fe}_2\text{OH}_2$	15.11±0.19		18.41±0.04		19.64±0.05	18.06±0.07	-1.3±2.0
	$\equiv\text{Fe}_2\text{O}_h\text{H}$	17.69±0.02		18.97±0.01		19.98±0.02	18.93±0.01	13.2±1.0

$\equiv\text{Fe}_2\text{O}_h\text{H}_2$	15.36 ± 0.26	18.45 ± 0.01	19.95 ± 0.01	18.19 ± 0.05	0.8 ± 1.7
H_3O^+	13.99 ± 0.12	18.38 ± 0.04	20.21 ± 0.05	17.95 ± 0.05	

REFERENCES CITED

- Cheng, J., Liu, X., VandeVondele, J., Sulpizi, M., and Sprik, M. (2014) Redox potentials and acidity constants from density functional theory based molecular dynamics. *Accounts of Chemical Research*, 47, 3522-3529.
- Cheng, J., and Sprik, M. (2012) Alignment of electronic energy levels at electrochemical interfaces. *Physical Chemistry Chemical Physics*, 14, 11245-11267.
- Cheng, J., Sulpizi, M., and Sprik, M. (2009) Redox potentials and $pK(a)$ for benzoquinone from density functional theory based molecular dynamics. *Journal of Chemical Physics*, 131, 154504.
- Costanzo, F., Sulpizi, M., Valle, R.G.D., and Sprik, M. (2011) The oxidation of tyrosine and tryptophan studied by a molecular dynamics normal hydrogen electrode. *The Journal of Chemical Physics*, 134, 244508.
- Liu, X., Lu, X., Sprik, M., Cheng, J., Meijer, E.J., and Wang, R. (2013) Acidity of edge surface sites of montmorillonite and kaolinite. *Geochimica et Cosmochimica Acta*, 117, 180-190.
- Sulpizi, M., and Sprik, M. (2008) Acidity constants from vertical energy gaps: Density functional theory based molecular dynamics implementation. *Physical Chemistry Chemical Physics*, 10, 5238-5249.