

Polaron Transport in Metal Oxides: A Frontier for Computational Chemistry

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and

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Iron Oxides act as the source/sink for soluble Fe in the environment

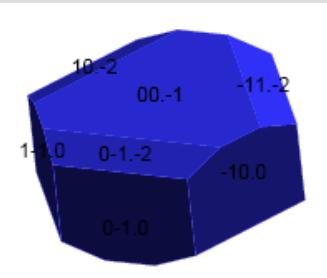
Iron bioavailability

Geochemical cycling of elements

Scavenging/Occlusion of other elements



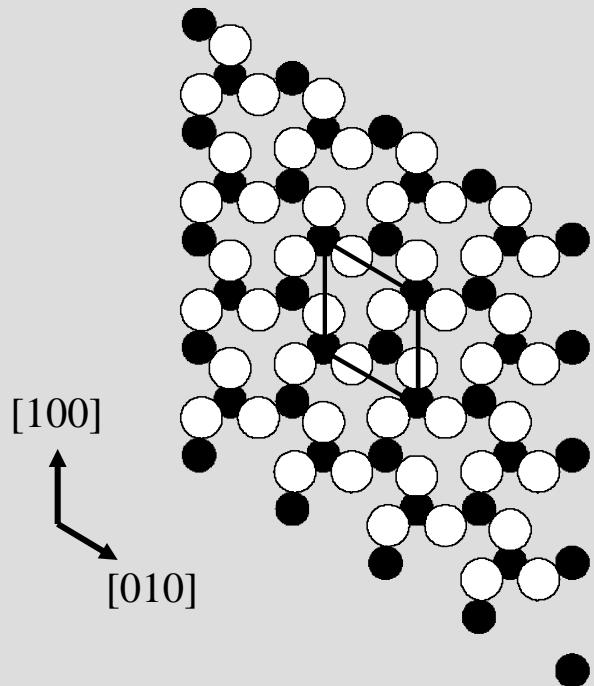
“Paint Pots”; Kootenay National Park, BC
A natural acid drainage system (pH 3-5)



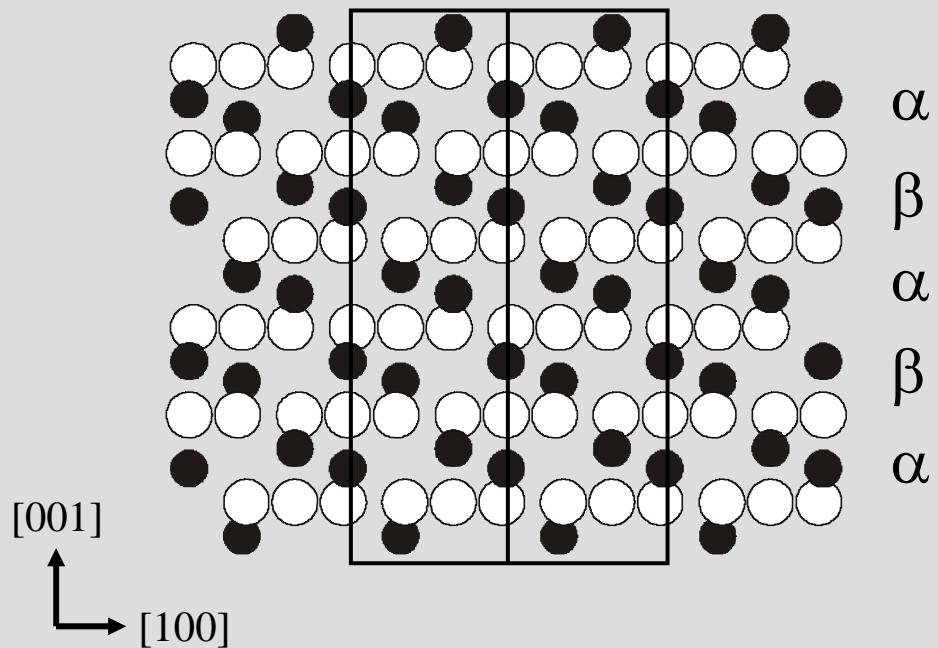
Hematite ($\alpha\text{-Fe}_2\text{O}_3$)

Corundum structure (R-3c)
High-spin Fe $3d^5$
AF (++ - -) / weakly FM

Charge transfer gap ($E_g \sim 2.2$ eV)
Highly anisotropic conductivity
Localized e^- (small polarons)

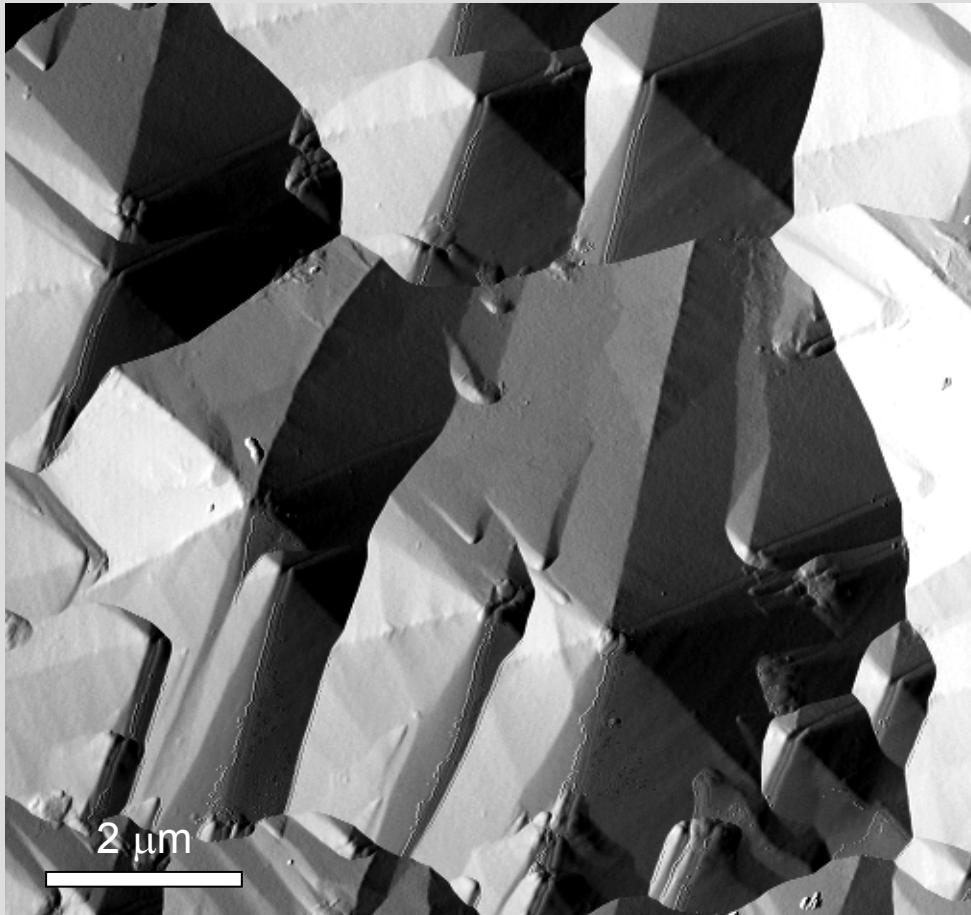
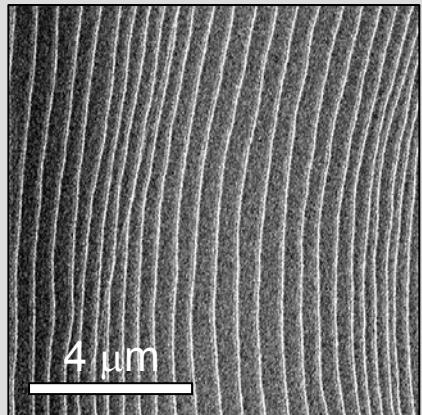


[001] zone view



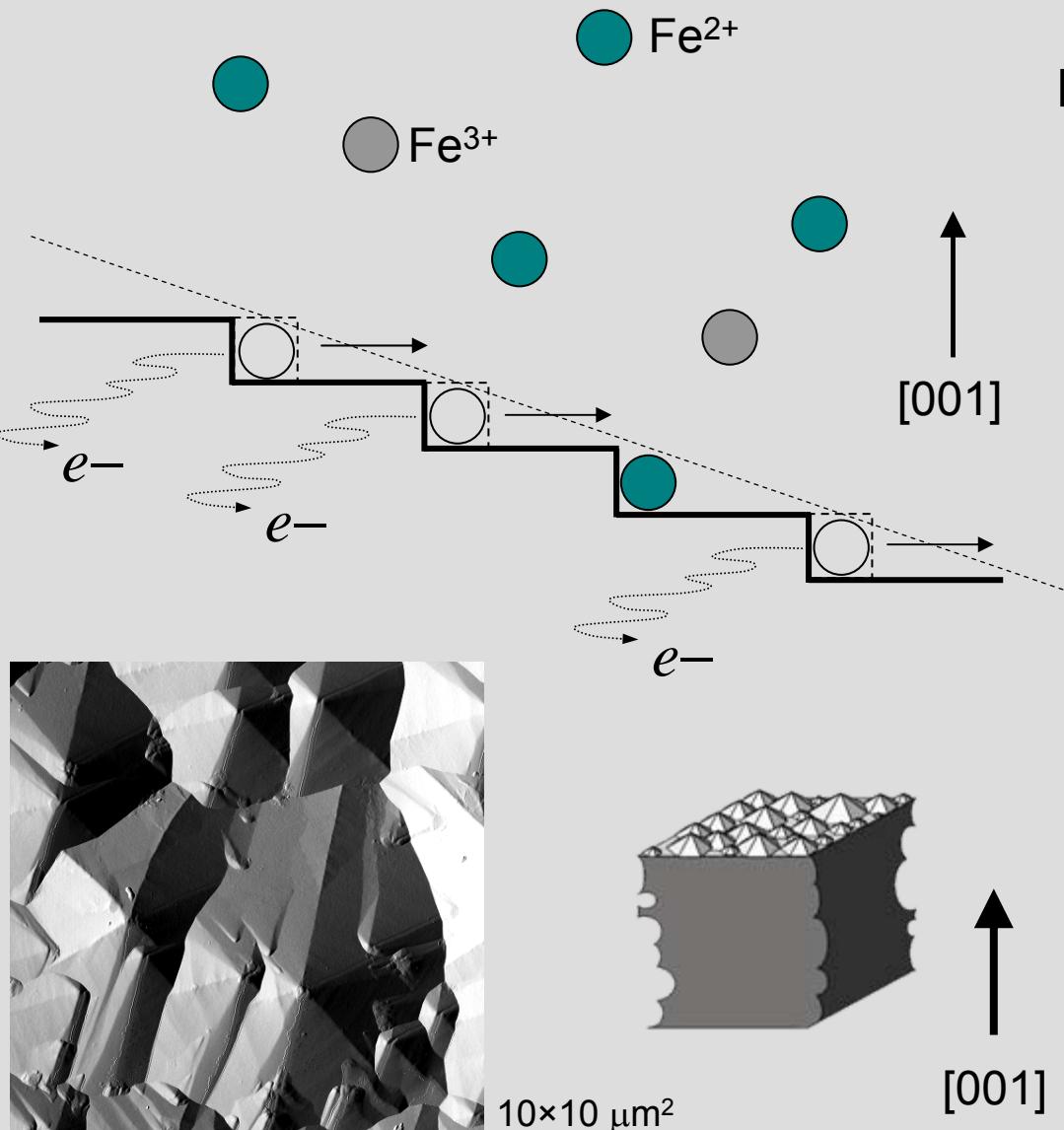
[110] zone view

Hematite (001) Reductive Dissolution by Fe(II) + Oxalate



Contact-mode deflection AFM image ($10 \times 10 \mu\text{m}^2$) after treatment in anoxic solution of 10^{-3} M $\text{FeCl}_2 + 10^{-3}$ M oxalic acid; pH = 2.8 (HCl) with 0.01 M NaCl at 75°C for 15 hours.

Coupled Dissolution / Electron Self-Diffusion



Electron Hopping
Diffusion Coefficient ($\mu\text{m}^2/\text{s}$):

AFM data $\sim 10^{-2}$

Theory = ?

Generalizations from AFM data:

Step height $\sim 3 \text{ \AA}$

Step density $\sim 2 / \text{nm}^2$

Attachment site density $\sim 2 / \text{nm}$

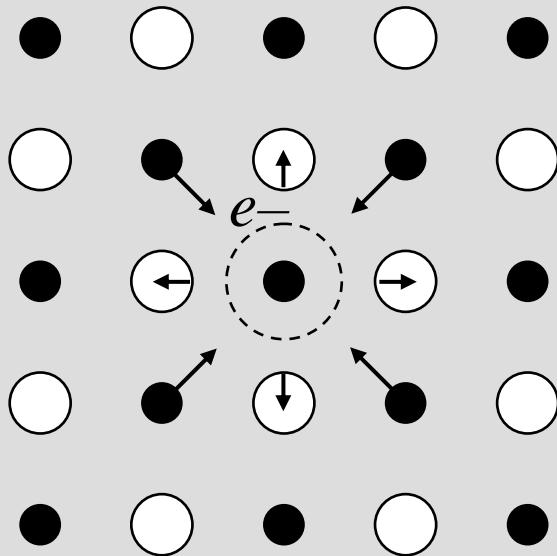
[001] growth rate $\sim 1 \text{ \mu m} / 12 \text{ hrs}$

Assumptions:

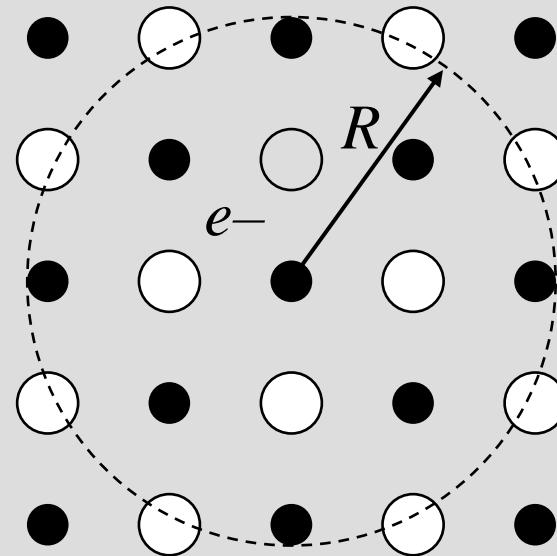
$\text{Fe}^{2+}_{(\text{aq})} \rightarrow \text{Fe}^{2+}_{(\text{ads})}$ $C_S \sim 0.01$

$\text{Fe}^{2+}_{(\text{ads})} \rightarrow \text{Fe}^{3+}_{(\text{s})}$ $\kappa \sim 0.01$

Electrons in Oxides - Polarons



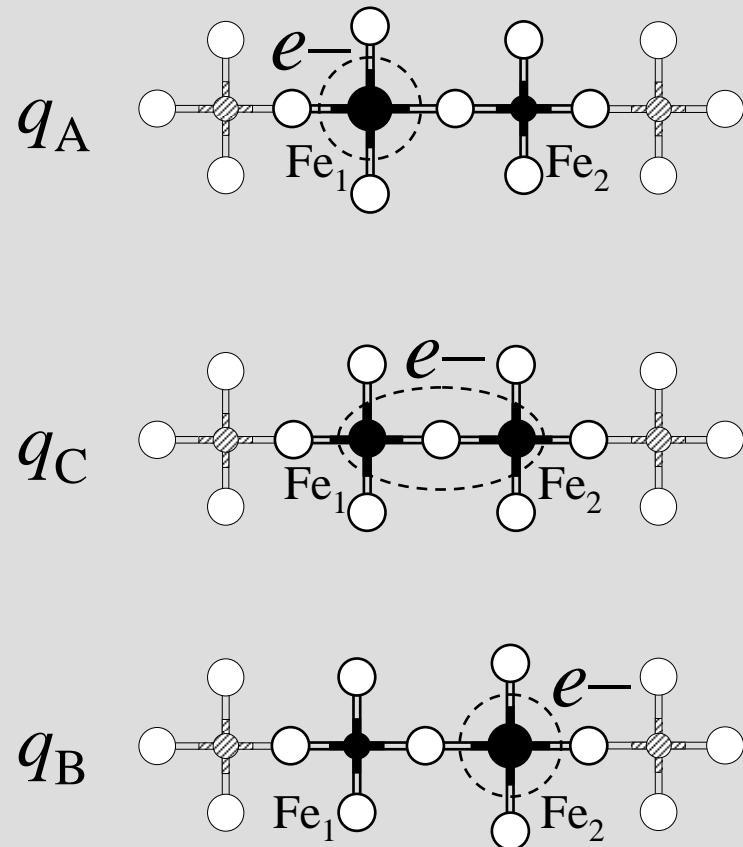
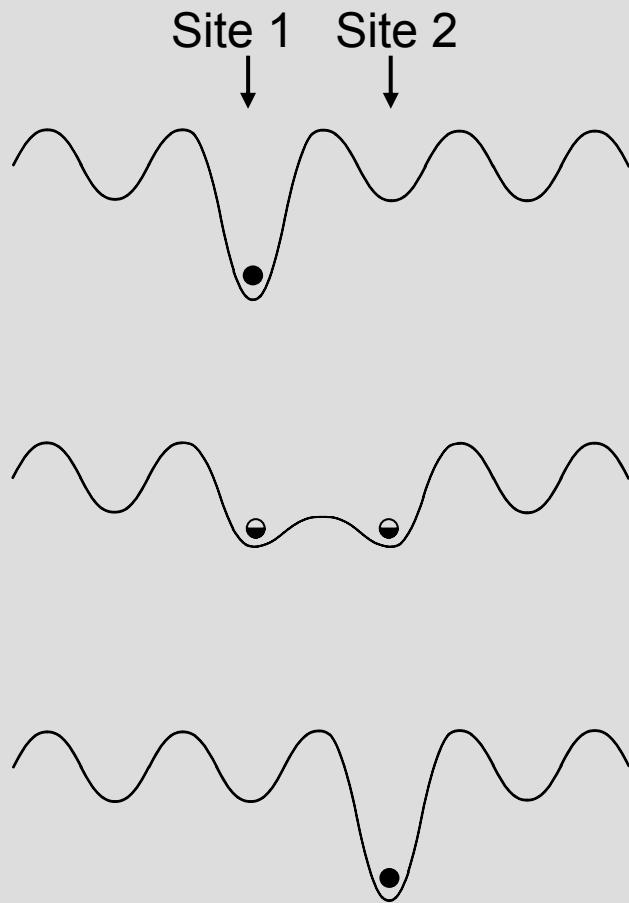
Small Polaron



Large Polaron

Modified from Cox (1987)

Polaron Hopping Model



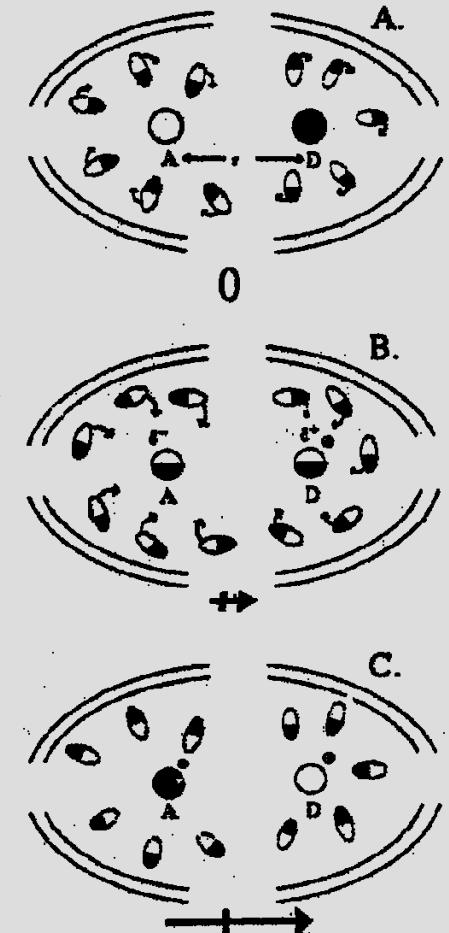
ET Theory – Reorganization Energy

- ▶ Usually separable into two main contributions
 - Internal component → bond reorganization

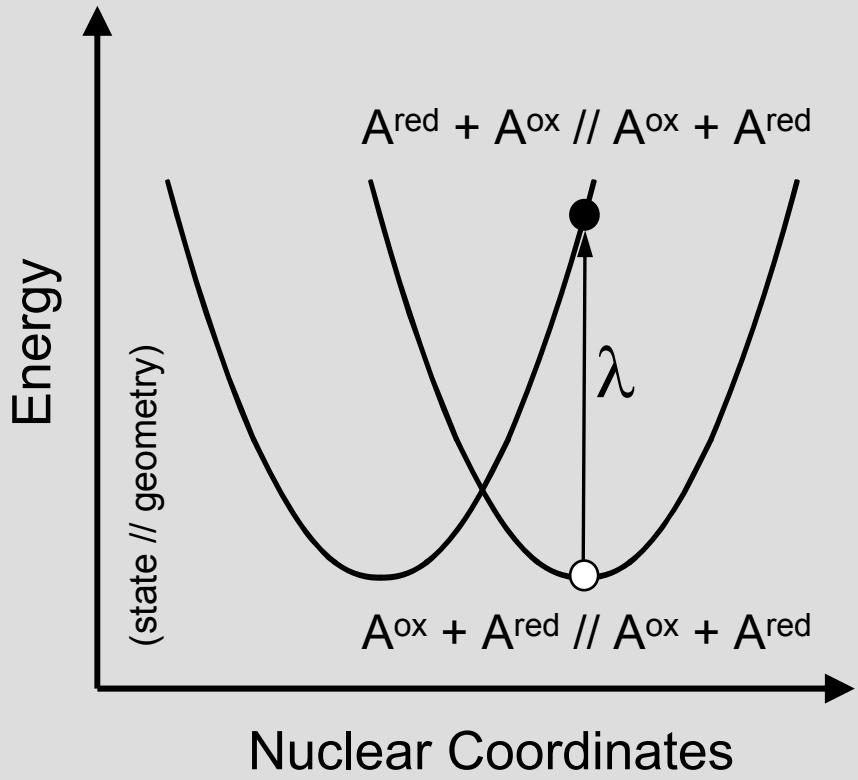
$$\lambda_I = \sum_j \frac{f_j^R f_j^P}{f_j^R + f_j^P} (\Delta q_j)^2$$

- External component → solvent re-orientation

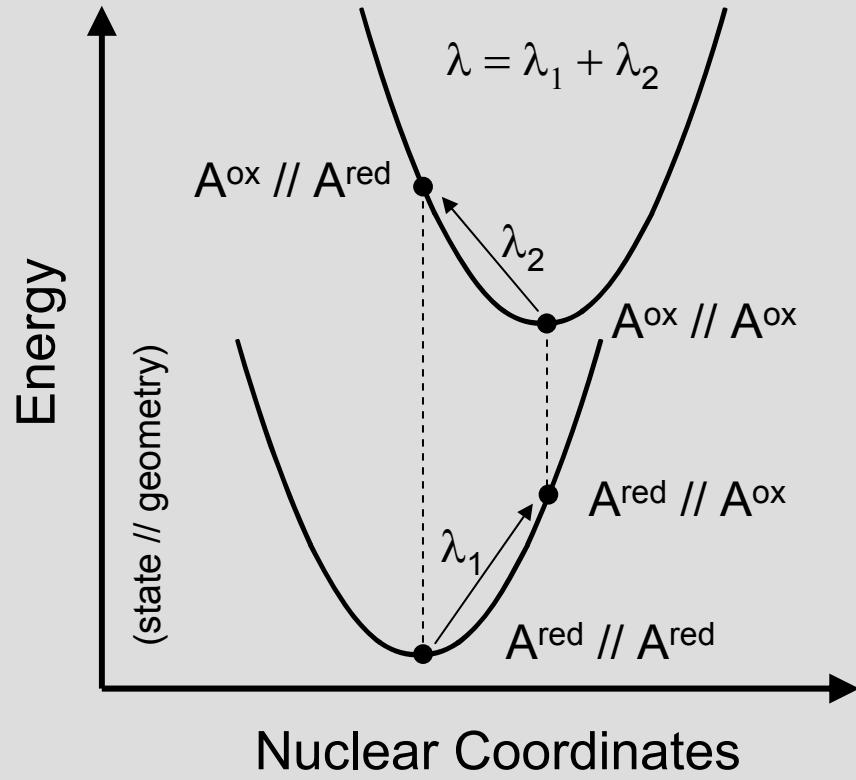
$$\lambda_E = (\Delta e)^2 \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{R} \right) \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right)$$



Methods for Computing the Reorganization Energy



Direct



4-Point

ET Theory – Electronic Coupling

- Quasi-diabatic approach:

$$V_{AB} = \frac{|H_{AB} - S_{AB}(H_{AA} + H_{BB})/2|}{1 - S_{AB}^2}, \quad \text{at } q_C$$

$$S_{AB} = \langle \psi_A | \psi_B \rangle, \quad H_{AA} = \langle \psi_A | H | \psi_A \rangle, \quad H_{BB} = \langle \psi_B | H | \psi_B \rangle, \quad H_{AB} = \langle \psi_A | H | \psi_B \rangle$$

- Generalized Mulliken-Hush approach:

$$V_{AB} = \frac{\mu_{12} \Delta E_{12}}{\sqrt{(\Delta \mu_{12})^2 + 4\mu_{12}^2}}, \quad \Delta \mu_{12} = \mu_{11} - \mu_{22}$$

μ_{12} = adiabatic dipole transition moment, ΔE_{12} = vertical excitation energy

ET Theory – Adiabaticity Criterion

- ▶ Transmission coefficient:

κ = overall probability (multiple passages through q_c)

$$\kappa = \frac{2P}{1+P}$$

P = the single event probability (each pass through q_c)

- ▶ Landau-Zener Model:

$$P = 1 - e^{-2\pi\gamma}$$

$$\gamma = \frac{2\pi V_{AB}^2}{h\nu_n |S_A - S_B|}$$

↗ PES slopes

- ▶ For identical parabolas (i.e., self-exchange):

$$P = 1 - e^{-\nu_{el}/2\nu_n}$$

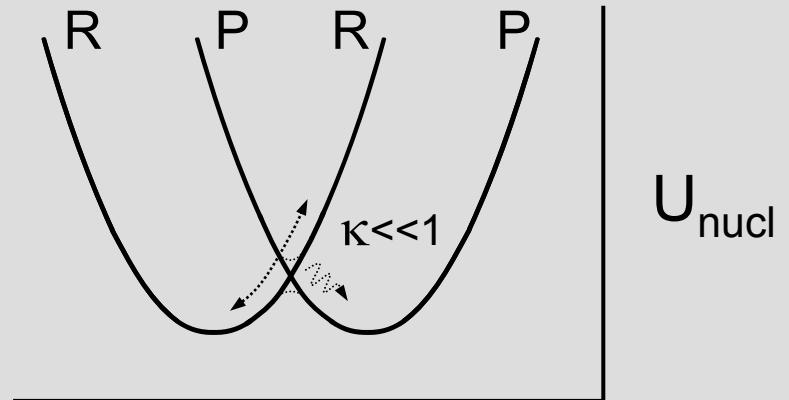
$$\nu_{el} = \frac{2V_{AB}^2}{h} \left(\frac{\pi^3}{\lambda RT} \right)^{1/2}$$

ET Theory – Rate Equations

Nonadiabatic ($\kappa \ll 1$)

$$k^{et} = \frac{2\pi}{\hbar} |V_{AB}|^2 \frac{e^{-(\Delta G^\circ + \lambda)^2 / 4\lambda RT}}{\sqrt{4\pi\lambda RT}}$$

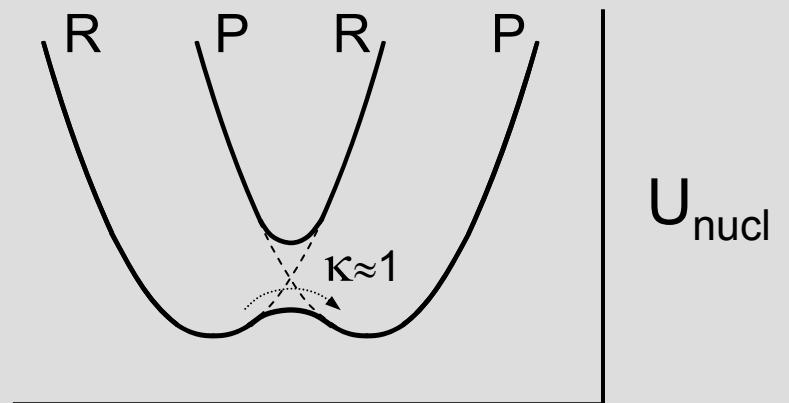
(*Fermi's Golden Rule*)



Adiabatic ($\kappa \approx 1$)

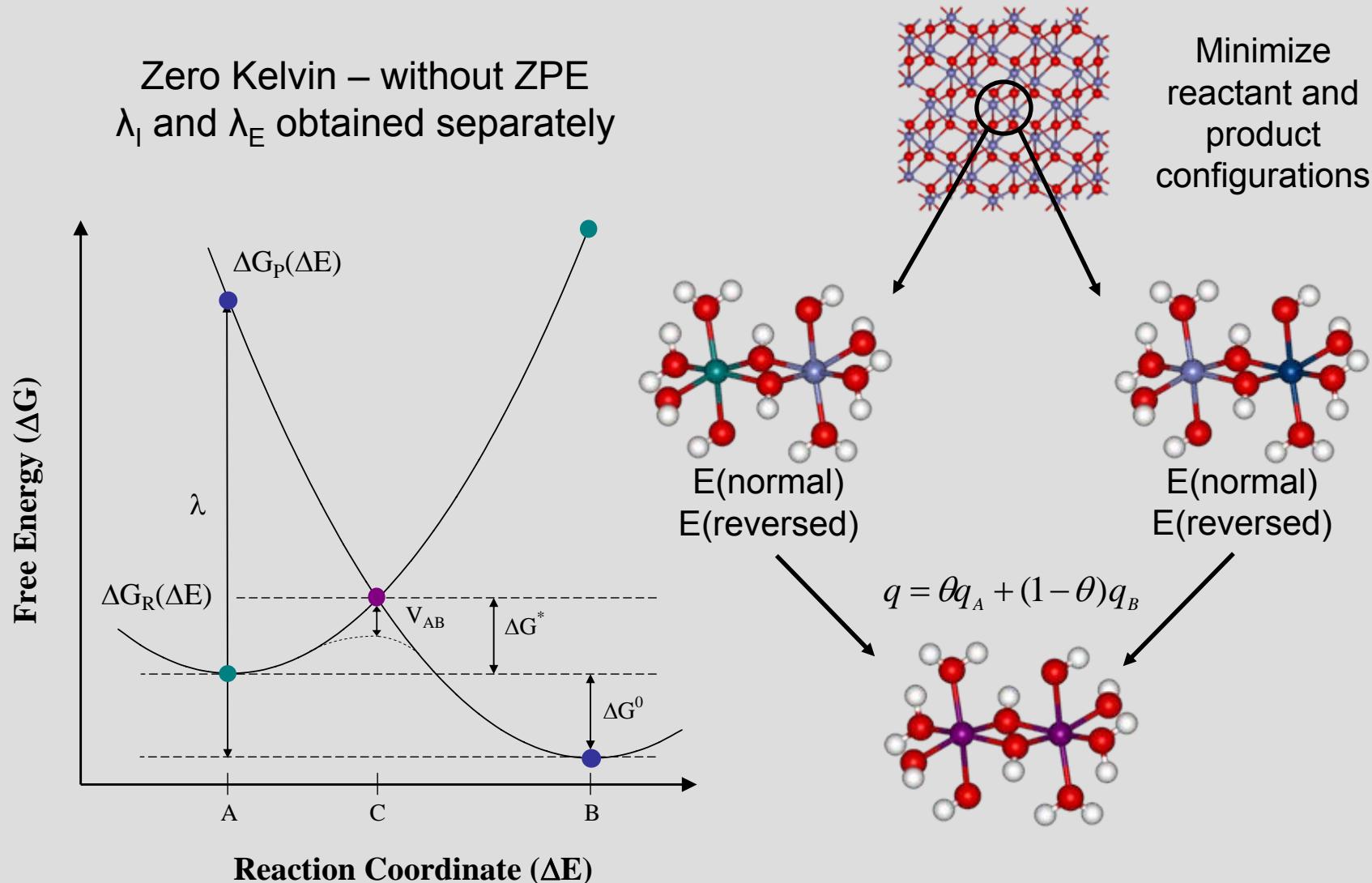
$$k^{et} = \Gamma \nu_n e^{(-\Delta G^*/RT)}$$

(*Transition state theory*)

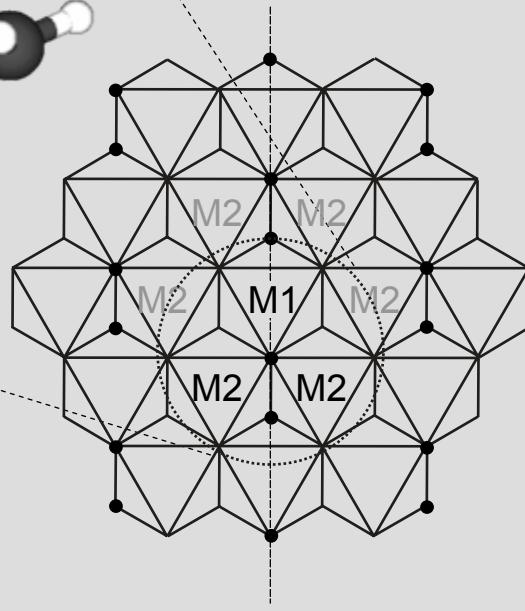
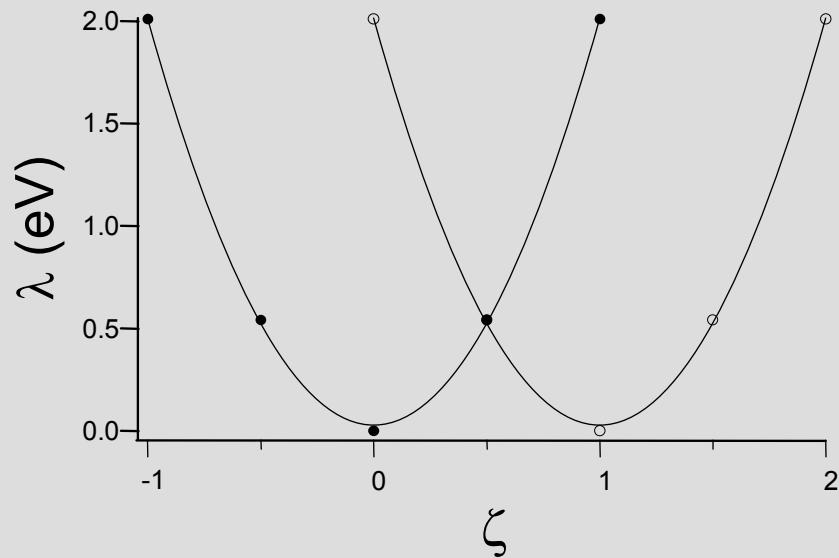
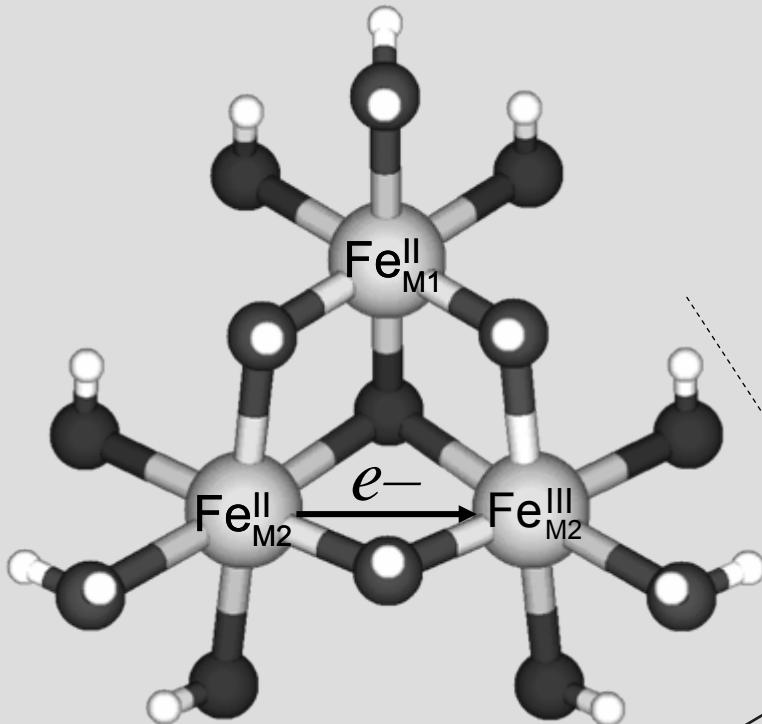


Nuclear Coordinates

Electron Transfer QM Cluster Approach



Edge-Sharing Trimer Model



NWChem
UHF
Ahrlrichs(Fe),6-311G(O,H)

M2 – M2

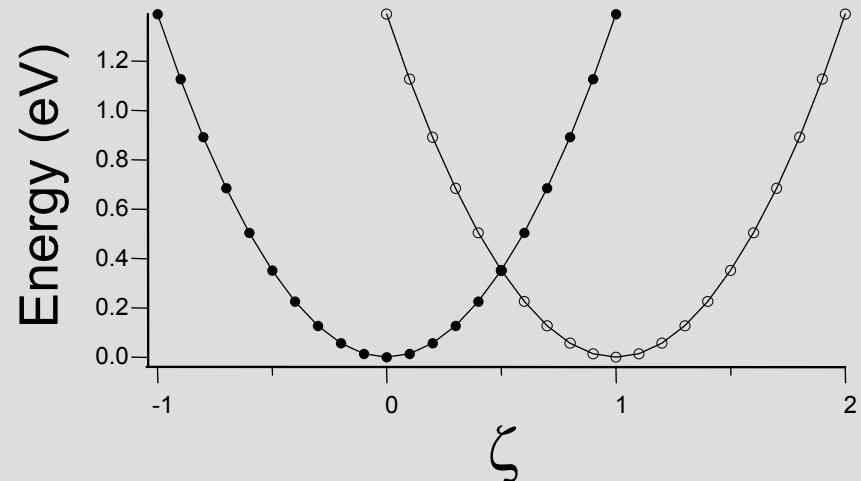
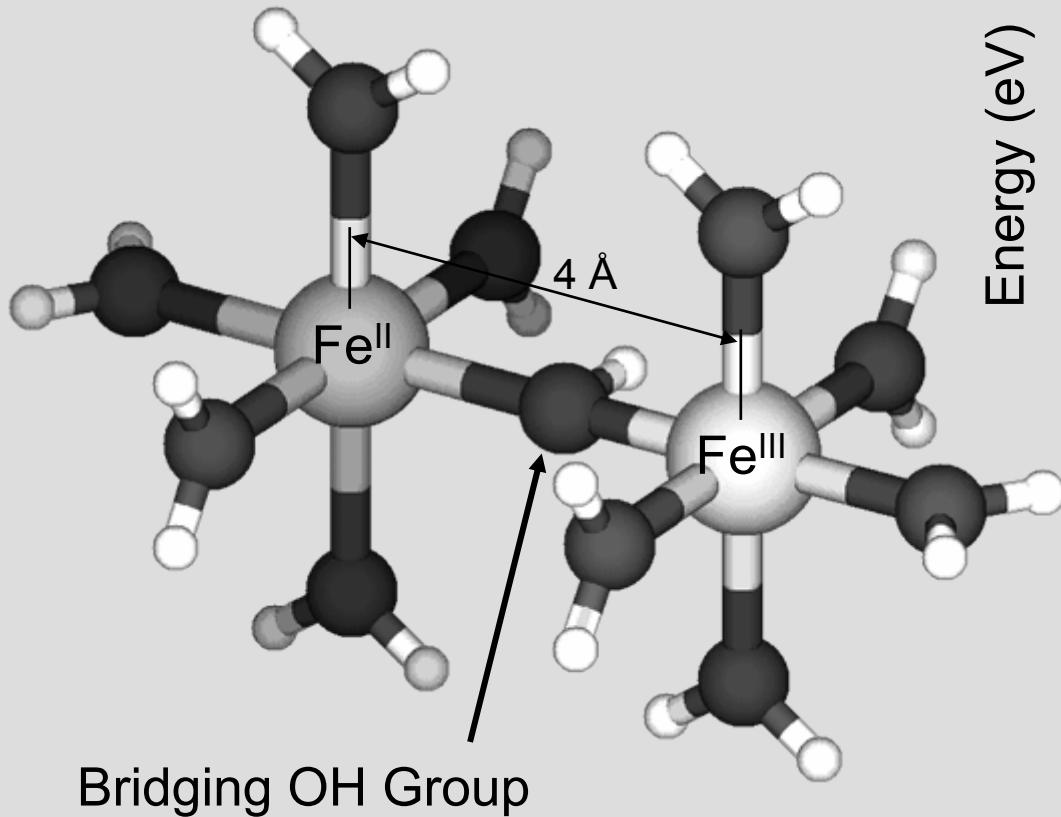
$$\lambda_I = 2.01 \text{ eV} \text{ (exp. } 1.7 \text{ eV)}$$

$$V_{AB} = 0.06 \text{ eV}, q = 0.5$$

$$\Delta G^* = 0.48 \text{ eV}$$

$$k_{et} = 8.3 \times 10^5 \text{ s}^{-1}$$

Corner-Sharing Dimer Model



Fe^{II}-O(H)-Fe^{III}

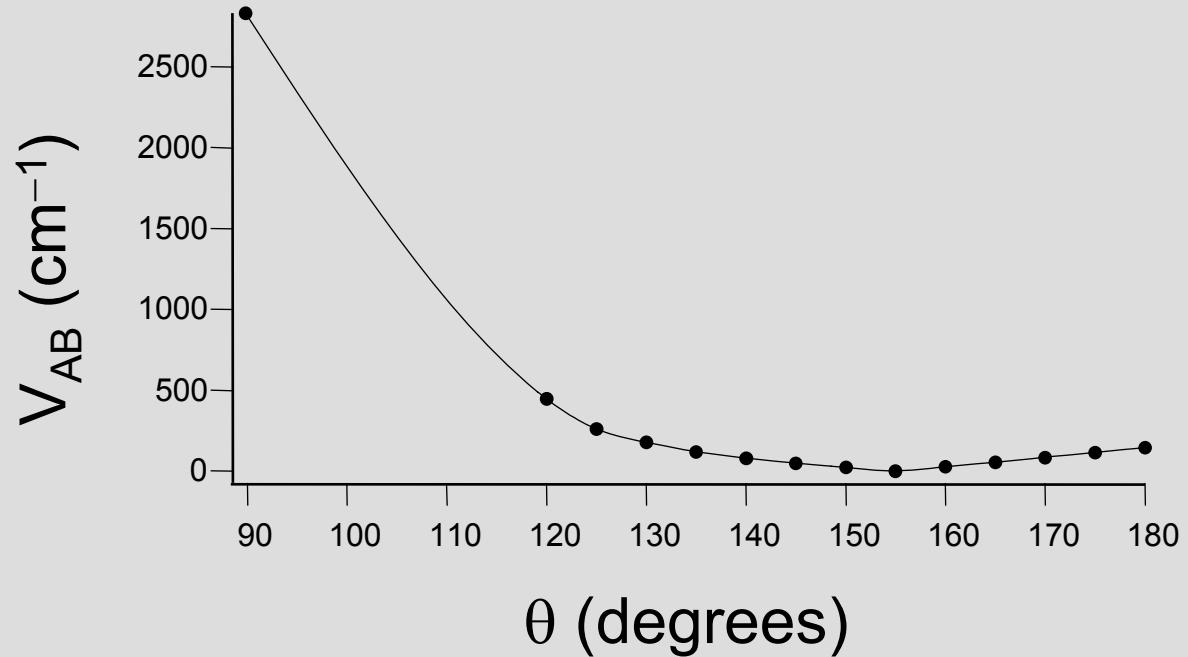
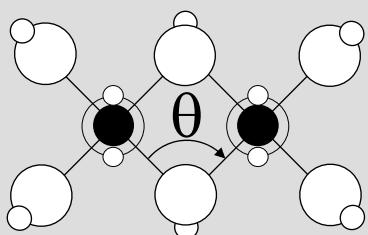
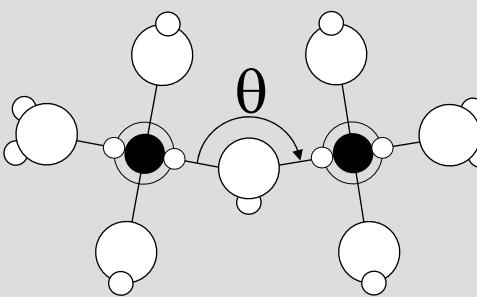
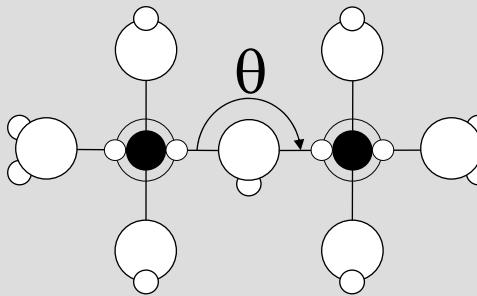
$$\begin{aligned}\lambda_I &= 1.40 \text{ eV} \\ V_{AB} &= 0.02 \text{ eV}, q = 0.5 \\ \Delta G^* &= 0.33 \text{ eV}\end{aligned}$$

$$k_{et} = 4.3 \times 10^6 \text{ s}^{-1}$$

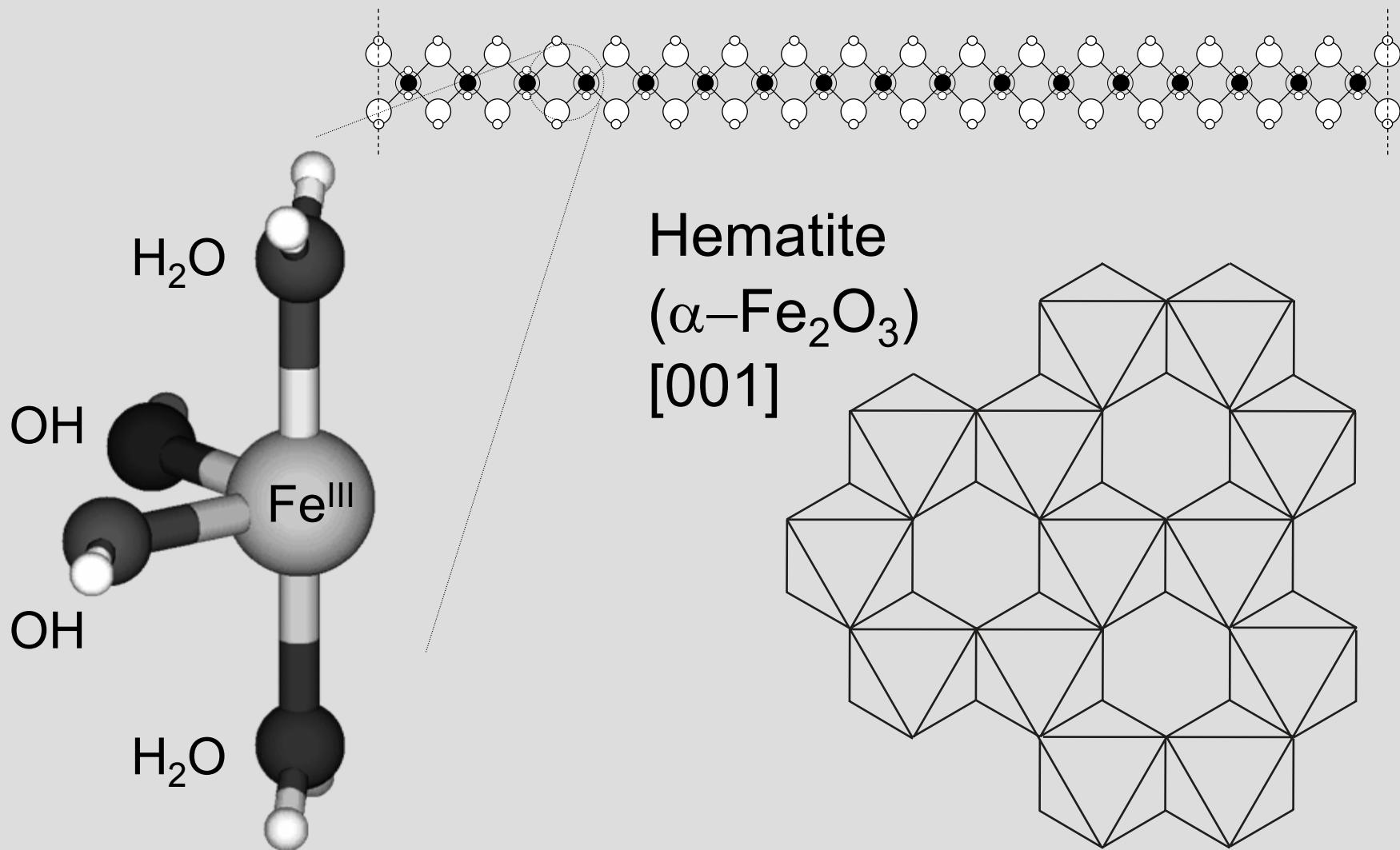
NWChem / UHF / Ahlrichs VTZ (Fe), 6-311++G** (O,H)

Rosso, Kerisit, Dupuis (2007) in prep.

Corner-Sharing Dimer Model Angular Dependence

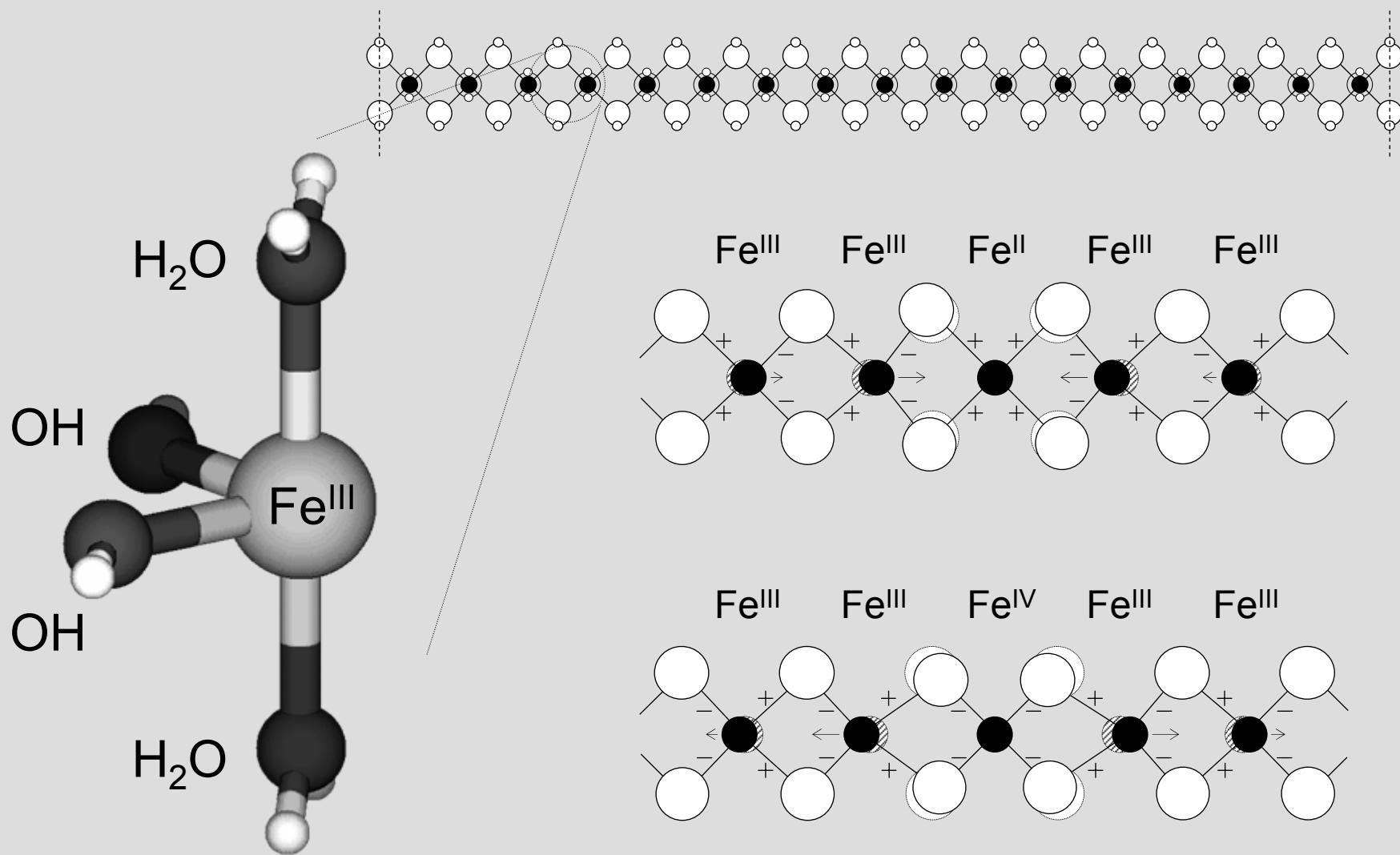


Edge-Sharing Chain Model:



Hematite
($\alpha\text{-Fe}_2\text{O}_3$)
[001]

Edge-Sharing Chain Model: Polaron Structure

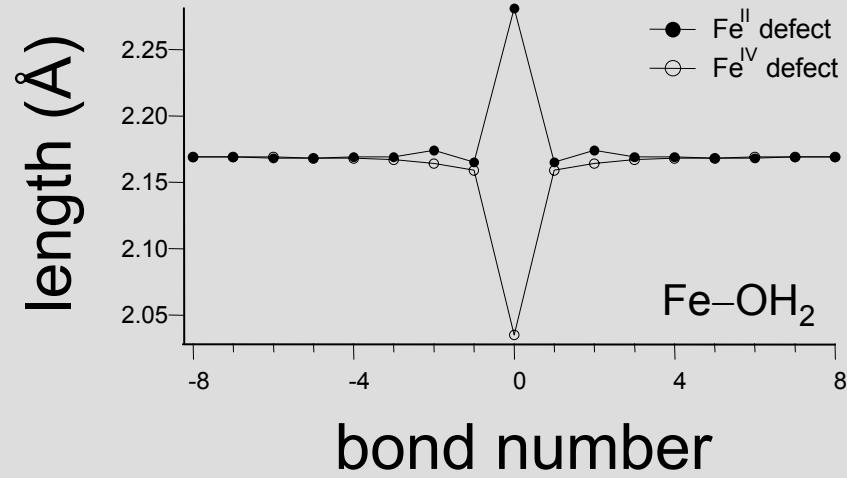
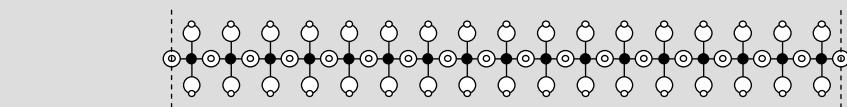
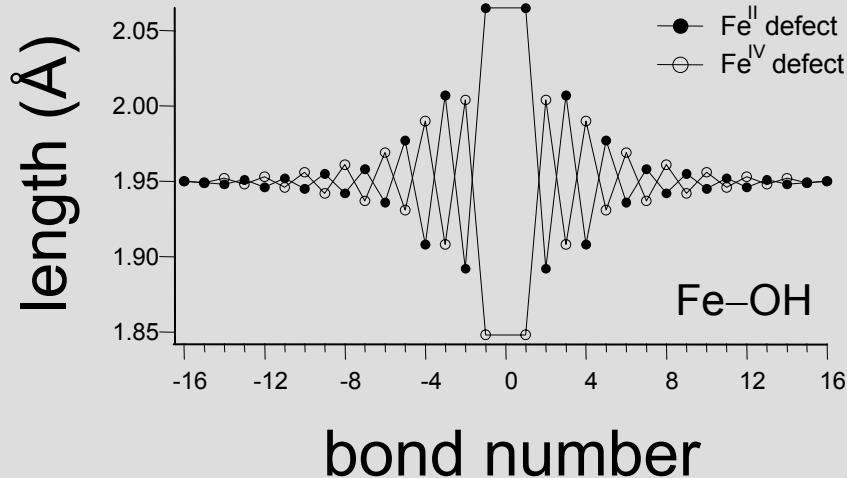
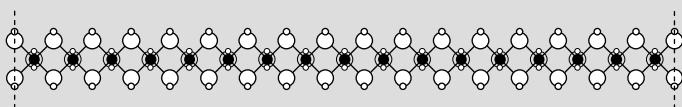
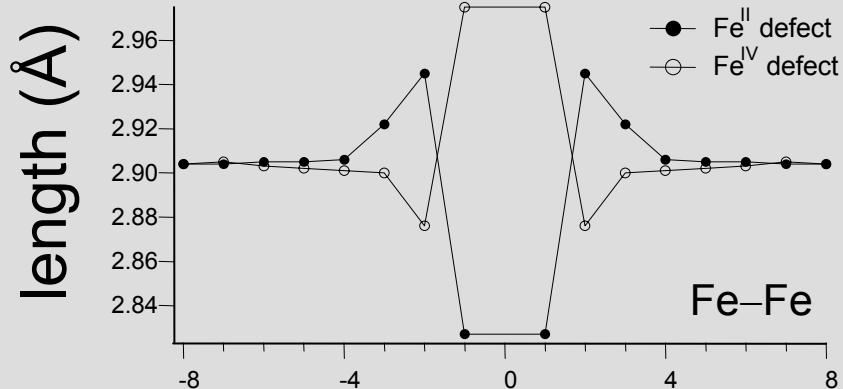


Edge-Sharing Chain Model: Polaron Structure

Crystal98

UHF

Durand and Barthelat ECP (Fe), 3-21G(O,H)



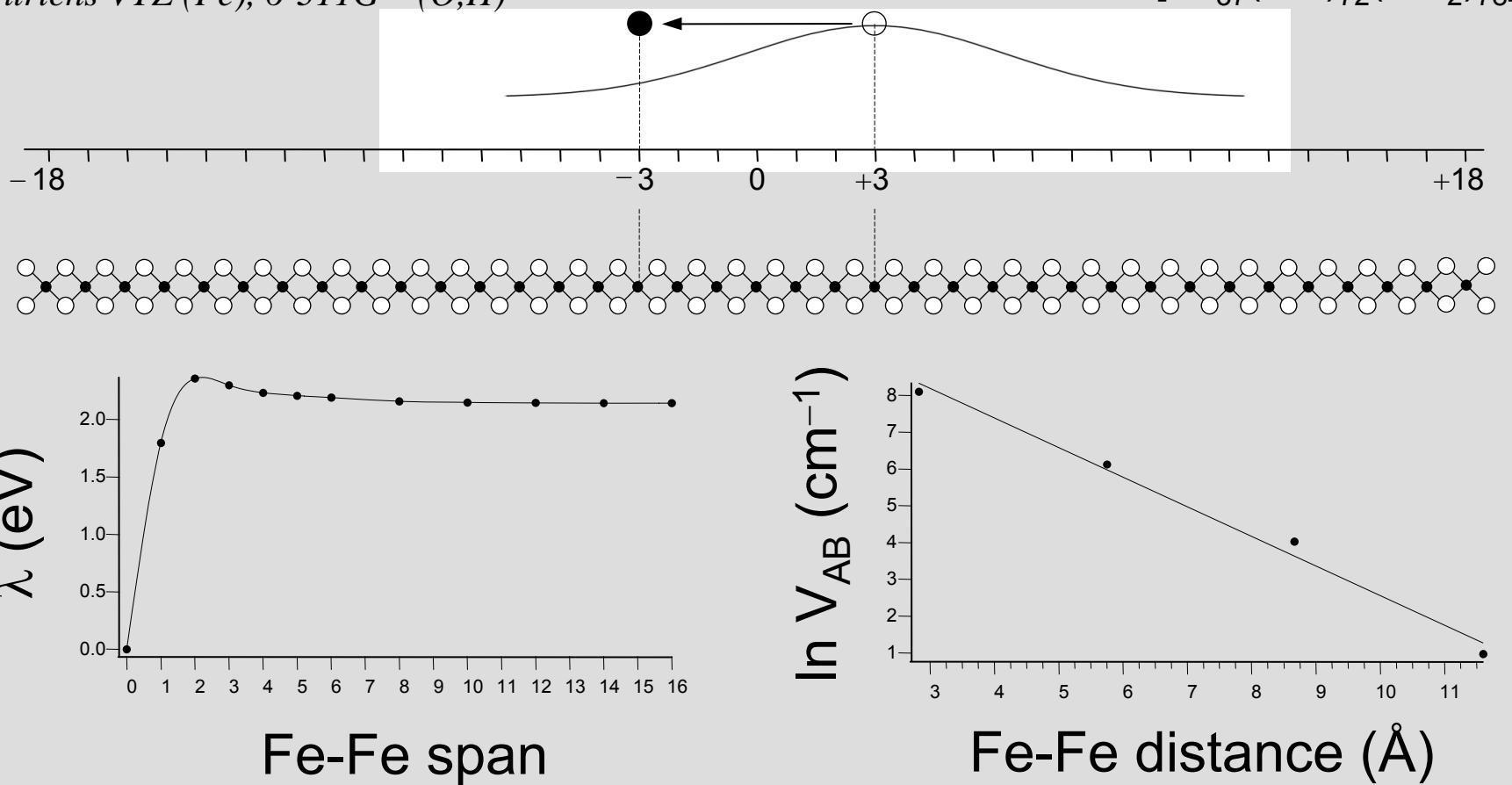
Edge-Sharing Chain Model: Calculated ET Quantities

NWChem

UHF

*Ahlrichs VTZ (Fe), 6-311G**(O,H)*

$[\text{Fe}_{37}(\text{OH})_{72}(\text{OH}_2)_{78}]^{+39}$



Nearest-neighbor ET: $\lambda_I = 1.80 \text{ eV}$; $V_{AB} = 0.41 \text{ eV}$, $\Delta G^* = 0.12 \text{ eV}$ (*exp.* 0.11 eV)

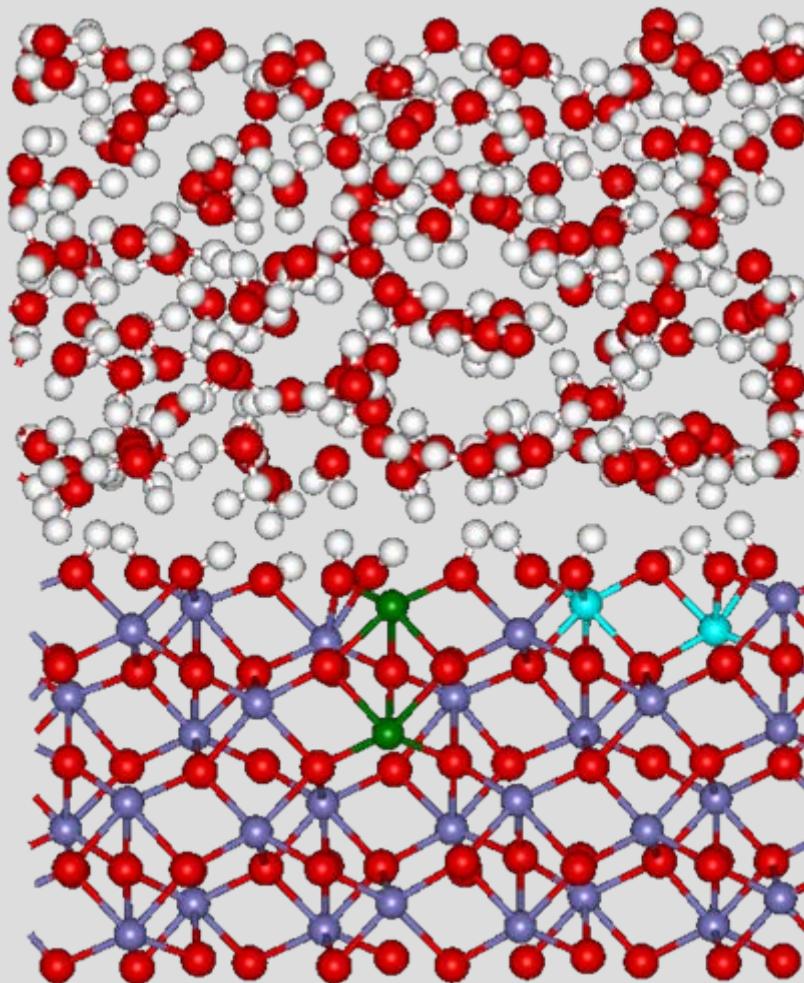
$$k_{\text{et}} = 3.5 \times 10^{12} \text{ s}^{-1}$$

Papaioannou et al. (2005)

Electron Self-Diffusion at Hematite Surfaces

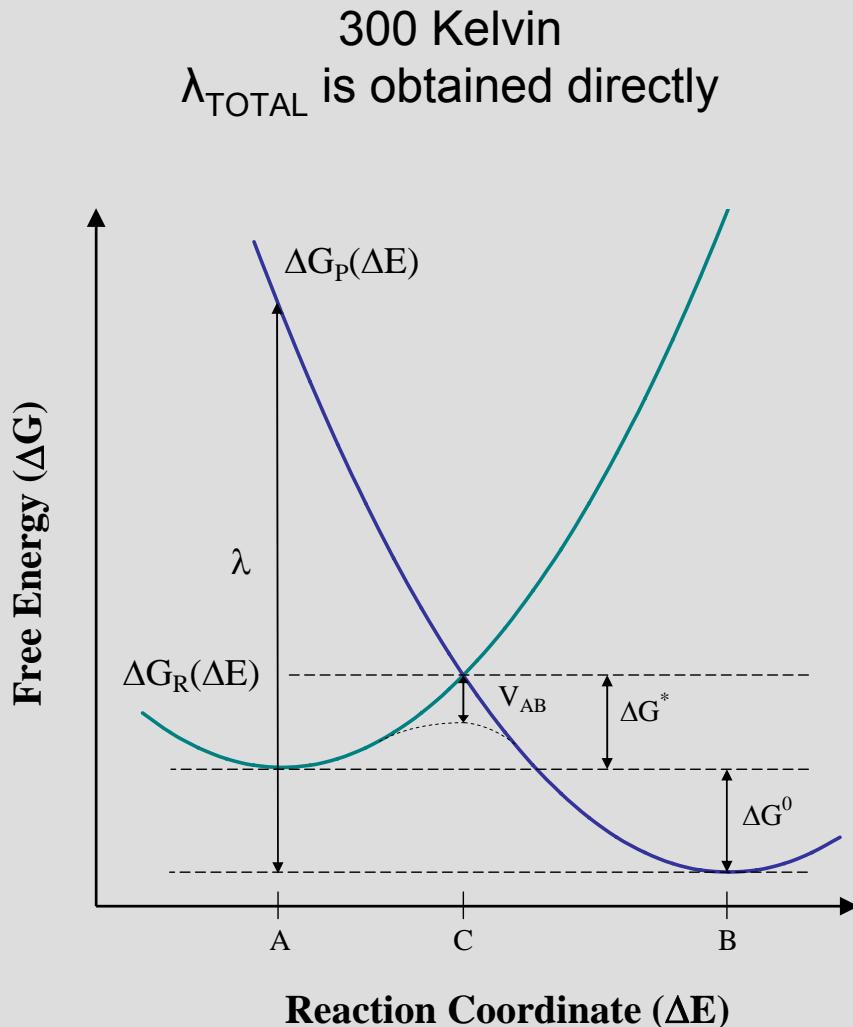
Hematite surfaces examined

Fe-terminated (001)
O(H)-terminated (001)
(012)



Hydroxylated hematite (001)

Electron Transfer MD + Umbrella Sampling



Run MD collecting configurations
 ΔE is calculated for each configuration

$$\Delta G(\Delta E) = -RT \ln \left[\frac{P(\Delta E)}{P(\langle \Delta E \rangle)} \right]$$

As configurations with $\Delta E \sim 0$ are rare, umbrella sampling technique is used to obtain a complete distribution.

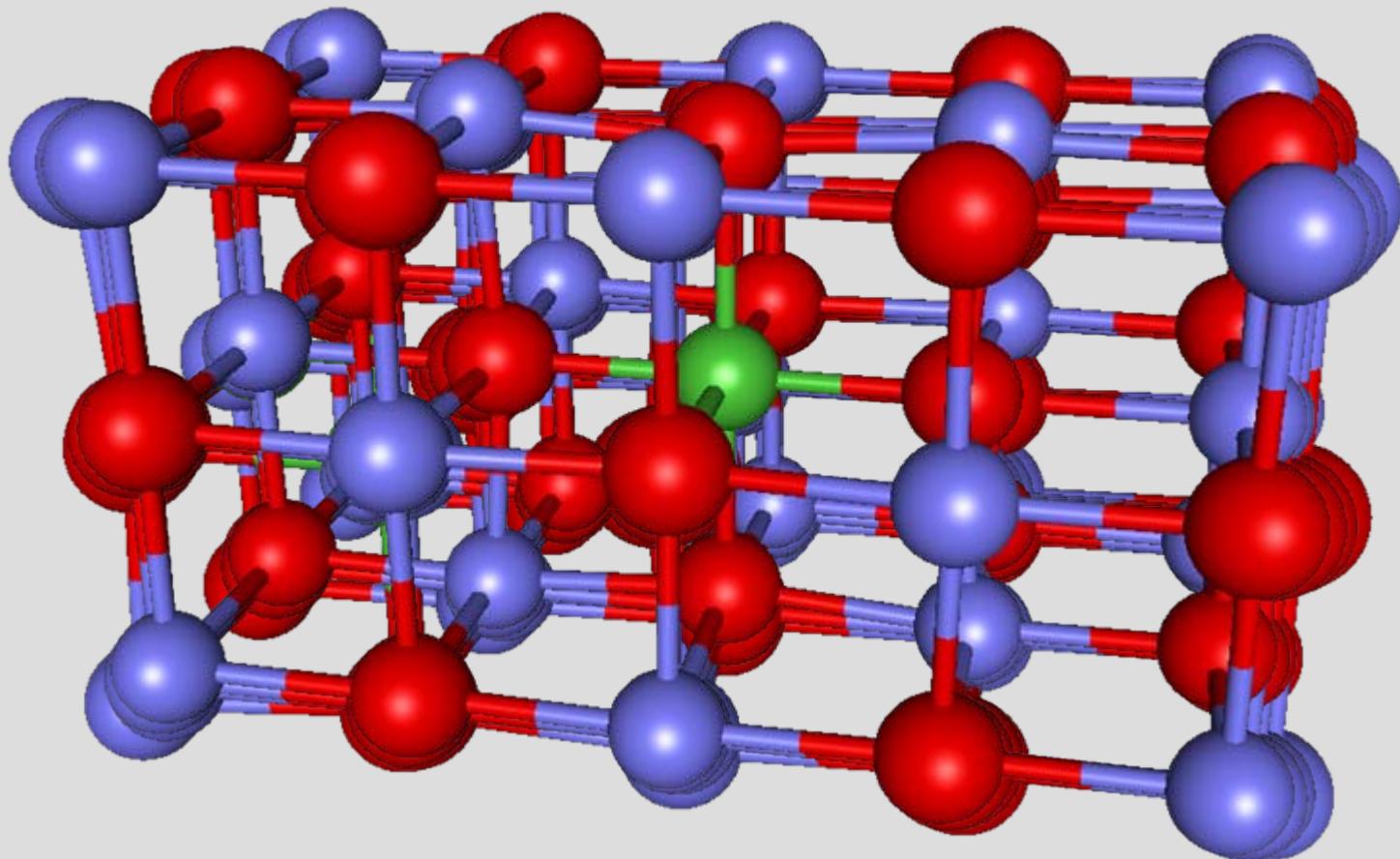
$$V_\theta = \theta V_A + (1 - \theta) V_B$$

Calculations are carried out for several values of θ (from 0 to 1).

Charge transfer in FeO: A combined molecular-dynamics and *ab initio* study

Sebastien Kerisit^{a)} and Kevin M. Rosso

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99352



MD and QM Methods Compared

Electron Hopping in Hematite

Direction	Model	λ (eV)	V_{AB} (eV)	ΔG^* (eV)	k_{et} (s^{-1})
Basal plane	MD	1.75	0.184	0.25	3.2E+09
Basal plane ^{1,2}	QM	1.42	0.190	0.19	3.4E+10
c direction	MD	1.88	0.028	0.44	6.5E+05
c direction ²	QM	1.47	0.028	0.34	3.3E+07

Electrical conductivity measurements on hematite single crystals show that conduction within basal plane is four orders of magnitude larger than conduction in c direction^{3,4}

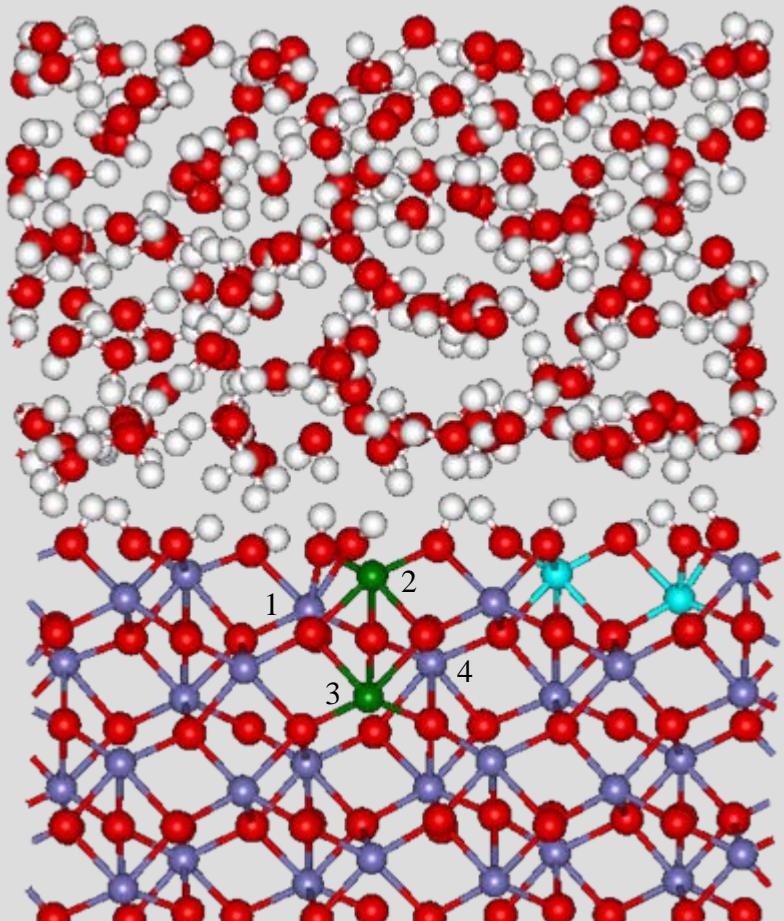
¹Rosso *et al.* *J. Chem. Phys.*, 118, 6455, 2003

²Iordanova *et al.* *J. Chem. Phys.*, 122, 144305, 2005

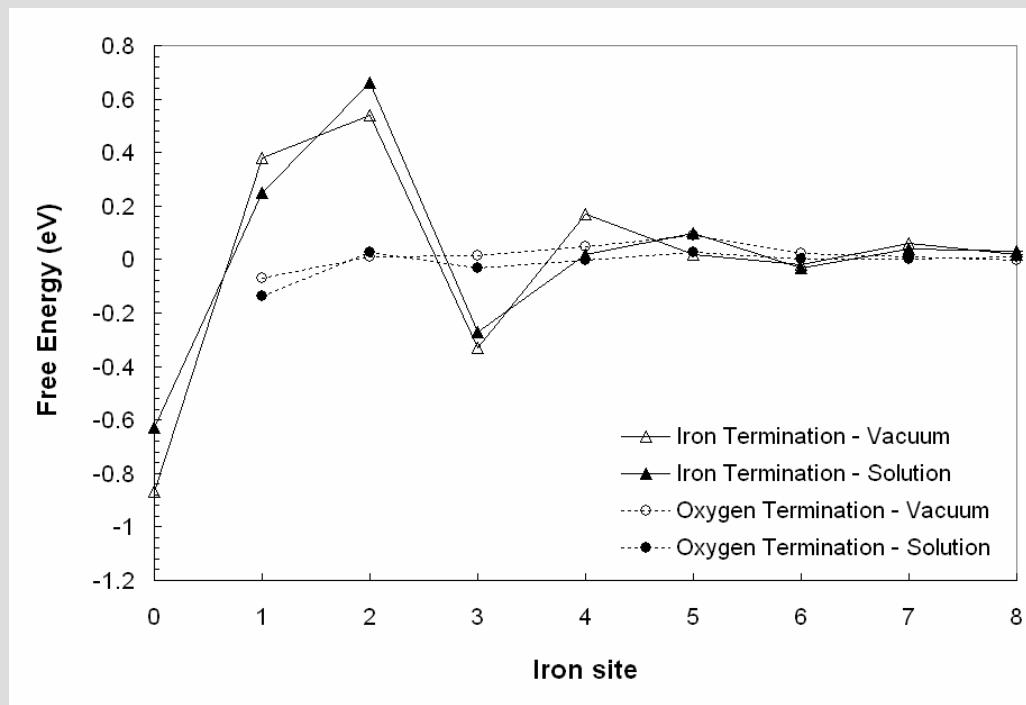
³Benjelloun *et al.* *Mat. Chem. Phys.*, 10, 503, 1984

⁴Nakau, *J. Phys. Soc. Jpn.*, 15, 727, 1960

Electron Self-Diffusion at Hematite (001)



Hydroxylated (001)



Available online at www.sciencedirect.com



Geochimica et Cosmochimica Acta 70 (2006) 1888–1903

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Geochimica

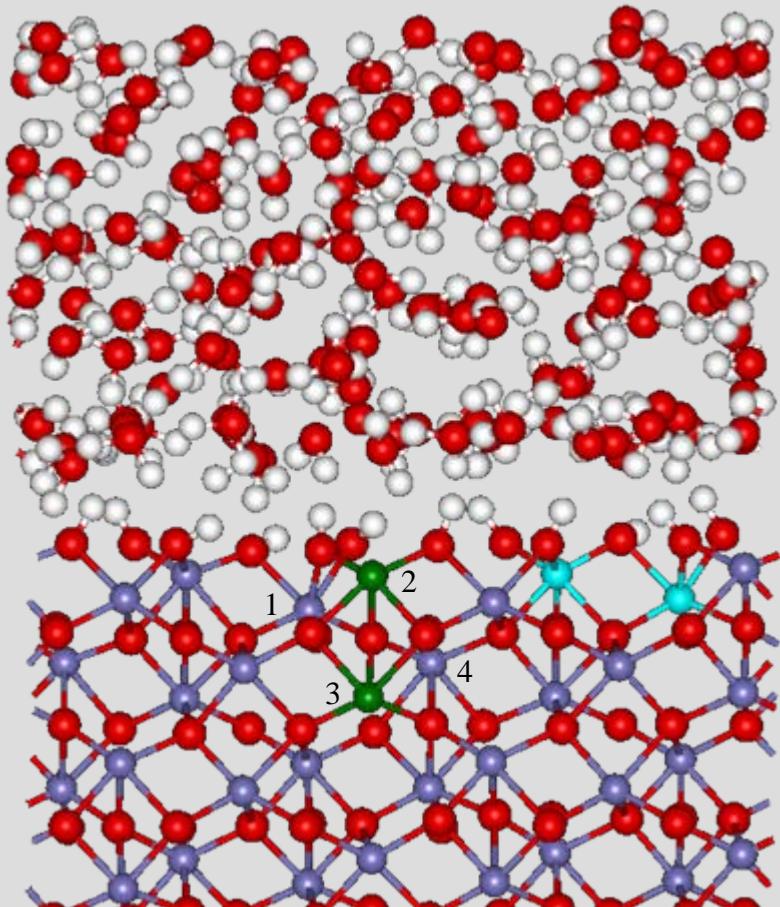
Computer simulation of electron transfer at hematite surfaces

Sebastien Kerisit *, Kevin M. Rosso

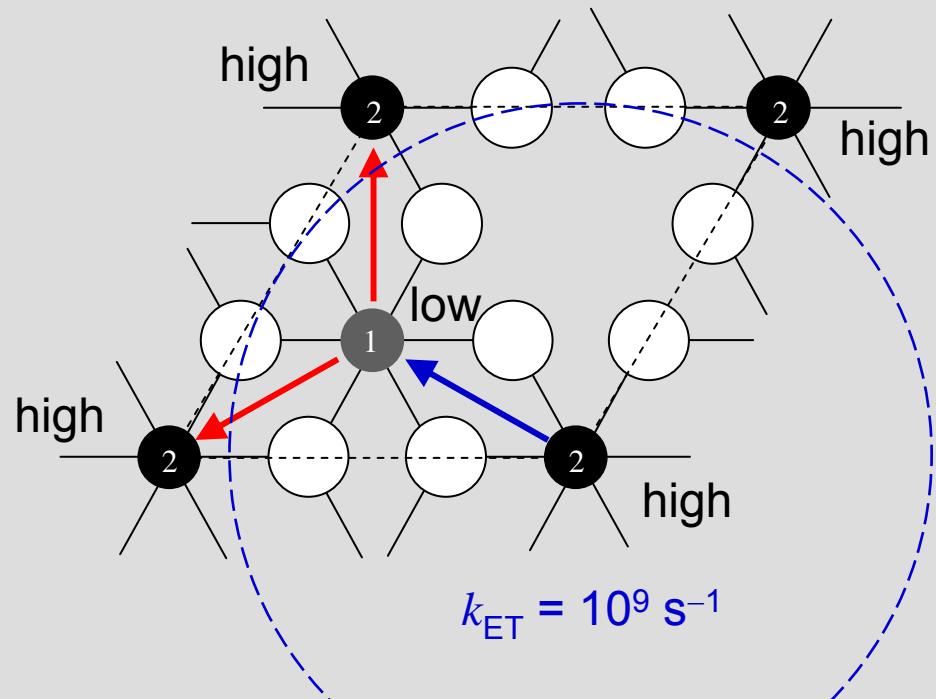
Chemical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352, USA

Received 2 September 2005; accepted in revised form 27 December 2005

Electron Self-Diffusion at Hematite (001)



Hydroxylated (001)



hydroxylated (001)

$$\Delta G^\circ = +0.16 \text{ eV}$$

$$k_{ET} = 10^7 \text{ s}^{-1}$$

$$D_{2D} = 10^{-1} \mu\text{m}^2 \text{ s}^{-1}$$

Electron Self-Diffusion at Hematite (001)

Layer(s)	Transfer	λ (eV)	V_{AB} (eV)	ΔG^0 (eV)	κ	i	ΔG^* (eV)	k (s ⁻¹)
<i>In vacuum</i>								
1	Basal-intra	2.20	0.017	-0.07	0.16	2	0.50	1.2E+05
1	<i>c</i> direction	2.17	0.028	0.01	0.35	1	0.52	3.1E+04
1–2	Basal-inter	1.81	0.184	0.33	1.00	1	0.45	5.7E+05
2	Basal-intra	1.72	0.184	-0.15	1.00	2	0.17	4.6E+10
2	<i>c</i> direction	1.91	0.028	-0.19	0.37	1	0.36	1.5E+07
2–3	Basal-inter	1.72	0.184	-0.02	1.00	1	0.24	1.9E+09
3	Basal-intra	1.70	0.184	0.06	1.00	2	0.27	9.2E+08
3	<i>c</i> direction	1.92	0.028	0.00	0.37	1	0.46	4.2E+05
<i>In solution</i>								
1	Basal-intra	2.15	0.031	-1.09	0.41	2	0.10	7.7E+11
1	<i>c</i> direction	2.17	0.028	-1.12	0.35	1	0.10	4.0E+11
1–2	Basal-inter	1.75	0.184	0.15	1.00	1	0.33	4.5E+07
2	Basal-intra	1.77	0.184	-0.08	1.00	2	0.22	8.4E+09
2	<i>c</i> direction	1.92	0.028	-0.07	0.37	1	0.42	1.8E+06
2–3	Basal-inter	1.70	0.184	0.06	1.00	1	0.27	5.0E+08
3	Basal-intra	1.74	0.184	0.02	1.00	2	0.26	1.6E+09
3	<i>c</i> direction	1.86	0.028	0.01	0.37	1	0.44	7.5E+05

Collective Electron Self-Diffusion: KMC

Fixed hematite lattice

Nearest-neighbor hops are considered

Each iron atom has 3 neighbors in basal plane and 1 in [001] direction.

$$k_{et} = v_n \exp\left(-\frac{(\lambda + \Delta G^0)^2 / 4\lambda - V_{AB}}{k_B T}\right)$$

1. Generate list of rates
2. Select one event
3. Increment time by $\ln(x) / (\text{total rate})$

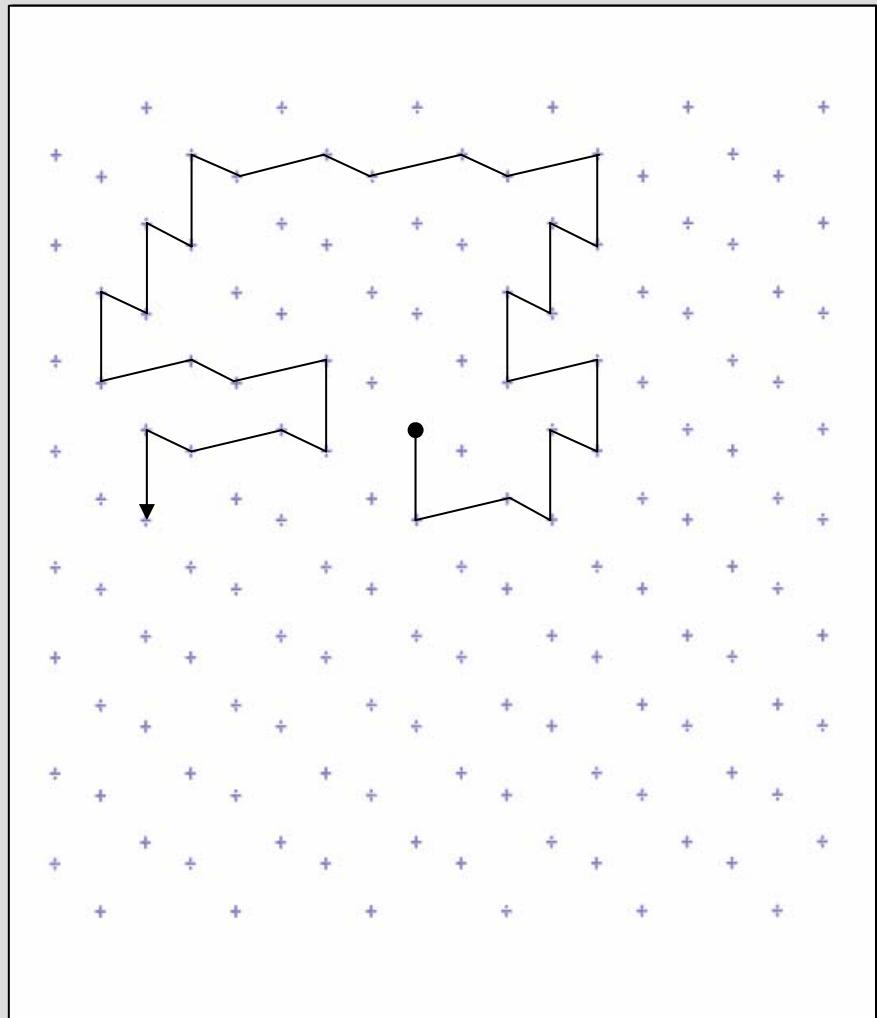
Diffusion coefficient is calculated from mean square displacement

$$D_{XYZ} = 44 \mu\text{m}^2/\text{s}$$

$$D_{\text{basal}} = 65 \mu\text{m}^2/\text{s}$$

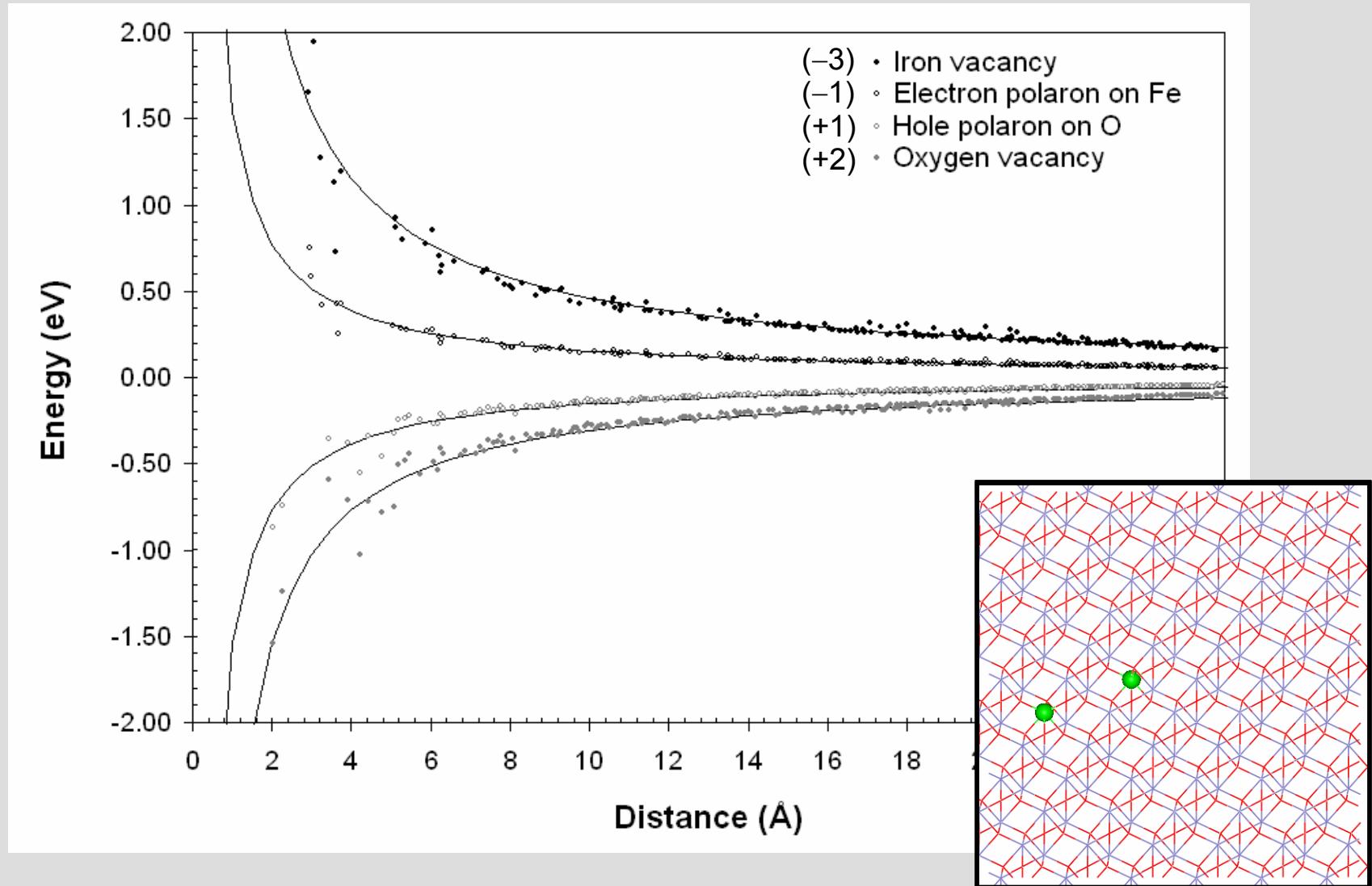
$$D_{[001]} = 0.03 \mu\text{m}^2/\text{s}$$

[001]



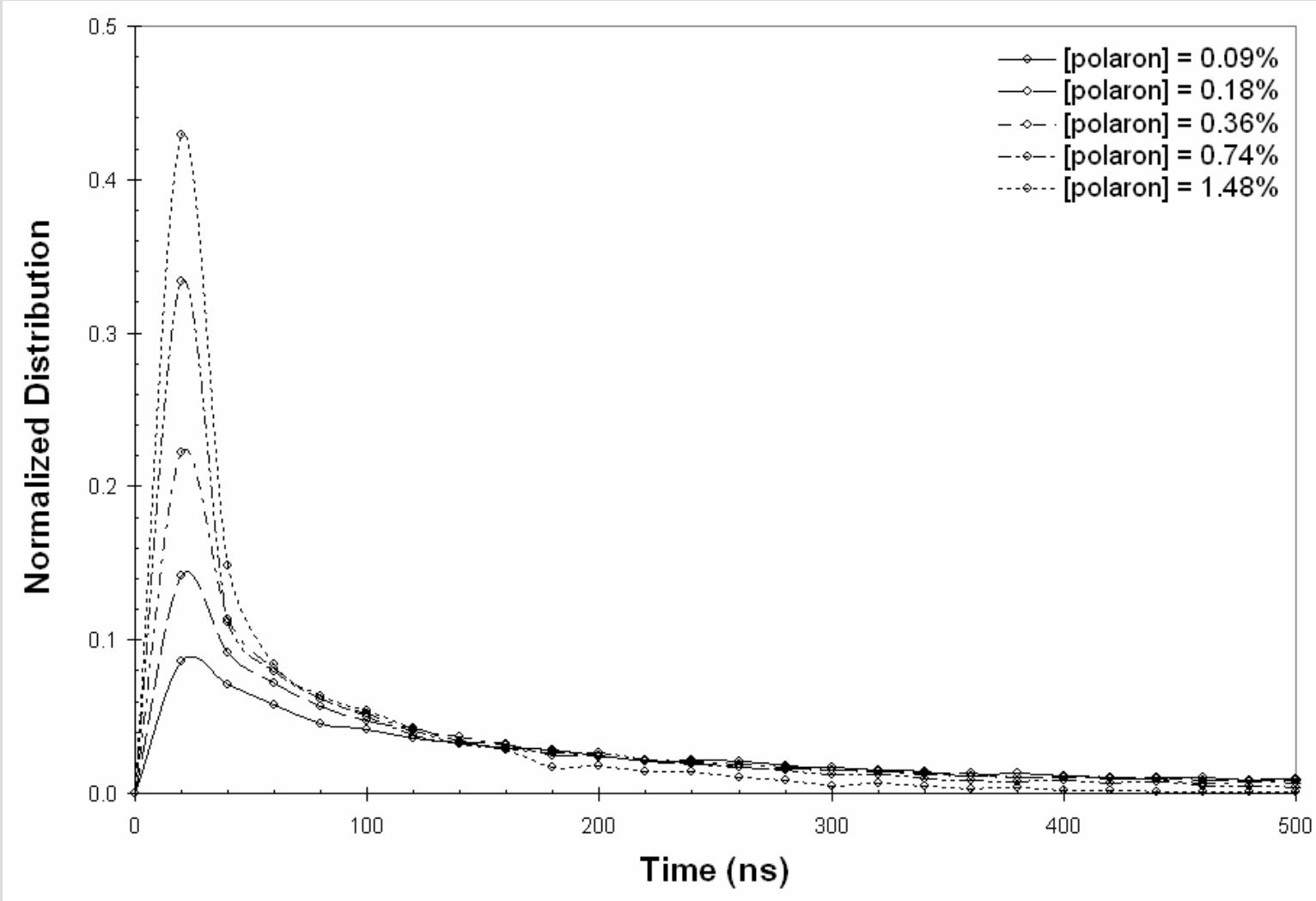
KMC Model: Polaron-Defect Interactions

MD-Based Interaction Potentials



Kinetic Monte Carlo Model

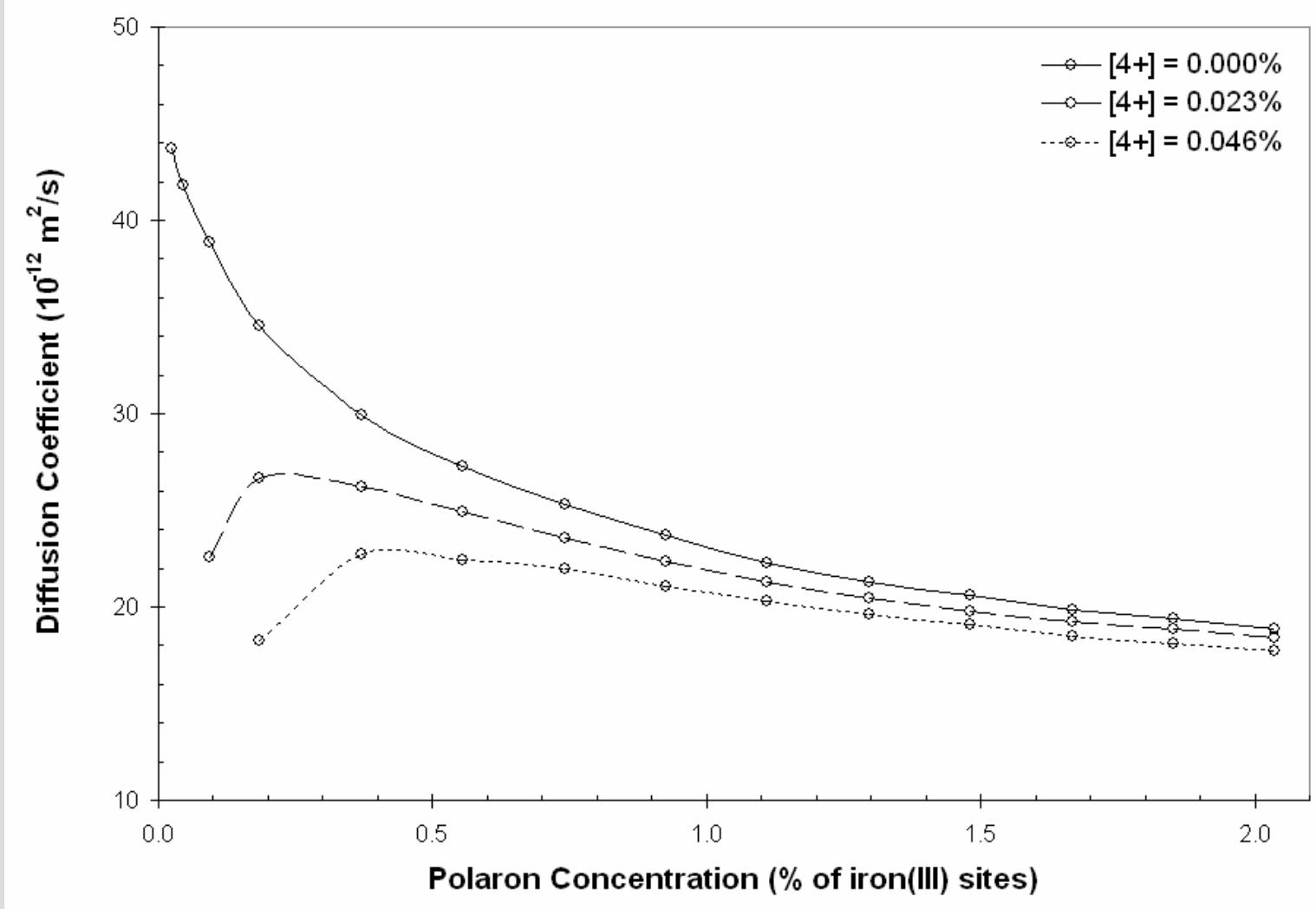
Residence time around Ti(IV) defect



+1 Defect at Fe Site \equiv Ti(IV)

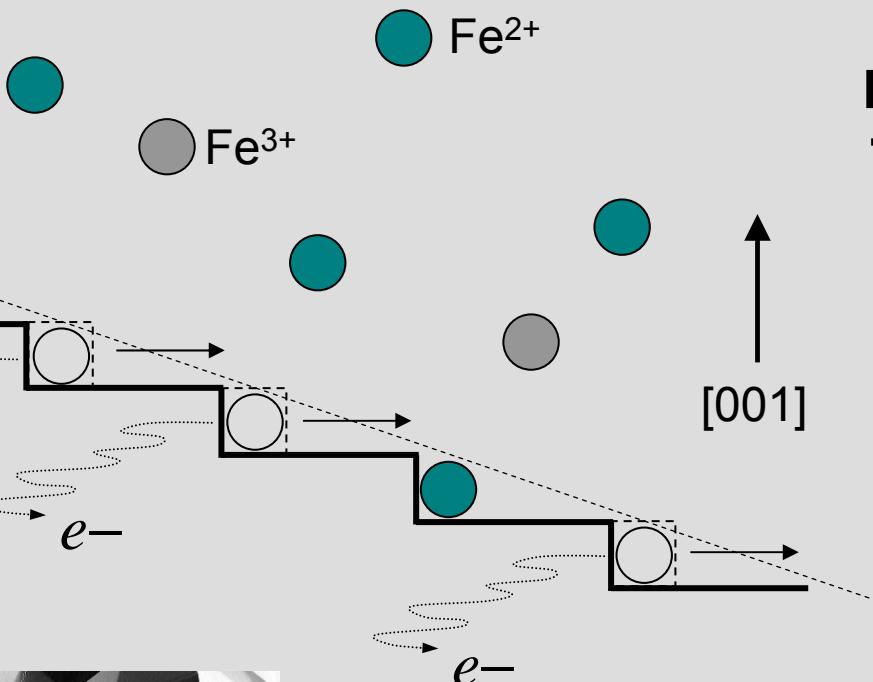
Kinetic Monte Carlo Model

Polaron diffusion parallel to (001) planes



+1 Defect at Fe Site \equiv Ti(IV)

Coupled Dissolution / Electron Self-Diffusion

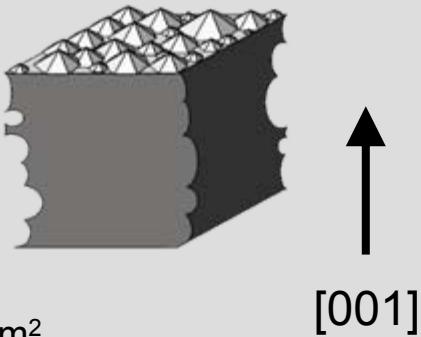
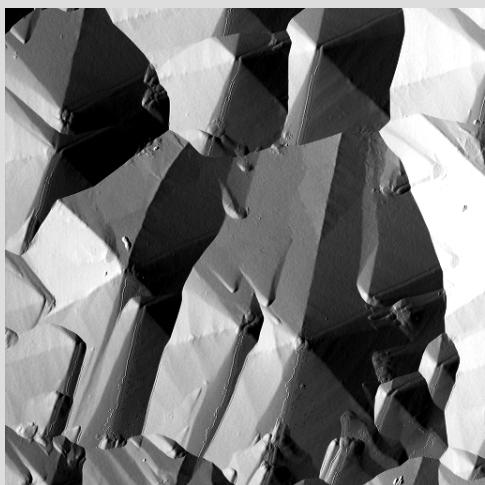


Electron Hopping Diffusion Coefficient ($\mu\text{m}^2/\text{s}$):

AFM data $\sim 10^{-2}$

Theory: 10^{-2} [001]
 10^1 (001)

$$D = \lim_{t \rightarrow \infty} \frac{1}{2t} \langle |r(t) - r(0)|^2 \rangle$$



Assumptions:

$\text{Fe}^{2+}_{(\text{aq})} \rightarrow \text{Fe}^{2+}_{(\text{ads})}$ $C_S \sim 0.01$
 $\text{Fe}^{2+}_{(\text{ads})} \rightarrow \text{Fe}^{3+}_{(\text{s})}$ $\kappa \sim 0.01$

Emerging Computational Needs

Tools for electron localization in DFT:

- exact exchange

- SIC

- constrained DFT

Efficient sampling schemes for evaluation of energy barriers:

- Transition path sampling

Other NWChem-specific upgrades:

- solid-state MD

- dielectric tensors from pspw

- MC toolbox

- LCAO periodic ab initio

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