Modeling cobalt porphyrin-catalyzed electrochemical reduction of CO_2 in water from first principles

SAND2012-8549C

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Acknowledgement

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KL also acknowledge Louise Criscenti, Pat Brady, and Susan Altman, and the US DOE Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences.

LDRD
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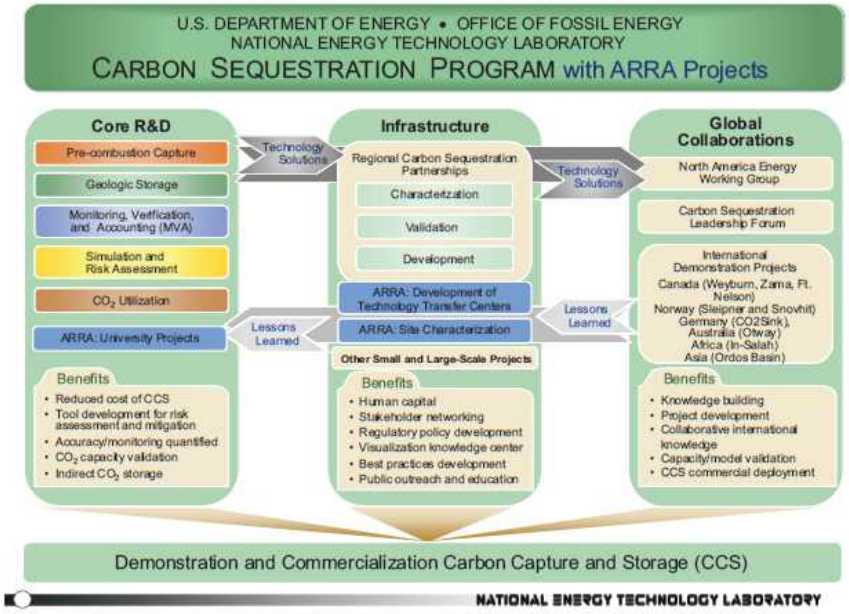
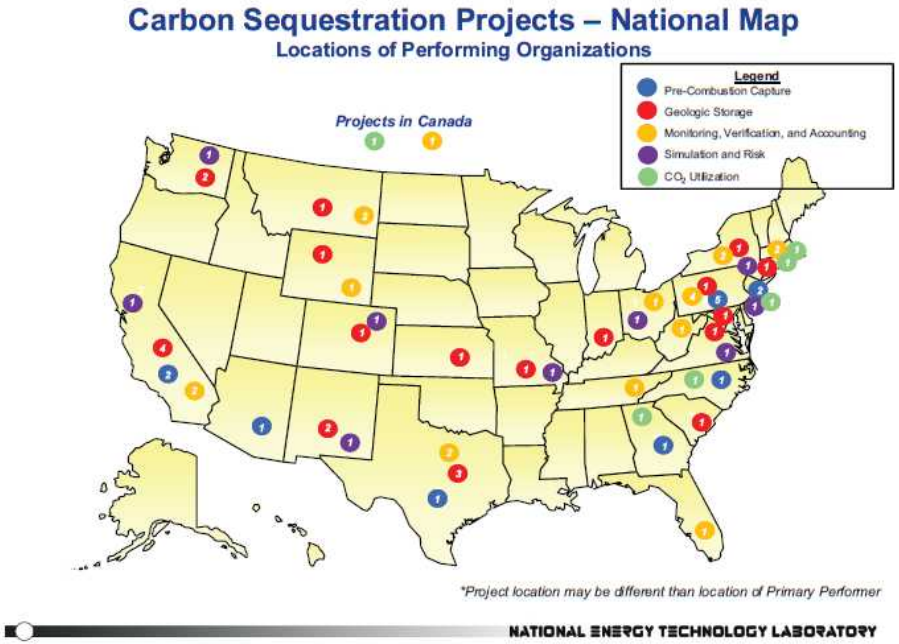
Sandia National Laboratories

Introducing the subject: CO_2 sequestration in the U.S.





CO_2 capture in SNL

Carbon Capture Research at Sandia National Laboratories

Sandia carbon capture research targets reuse (3 year Sandia Grand Challenge LDRD) and the fundamental and applied aspects of carbon capture for sequestration (funding sources are in parentheses):

- **Weathering/mineralization** (3 year ARPA-E with Columbia University) Accelerating silicate weathering to store CO_2 as a mineral,
- **Switchable polymers** (3 year Sandia LDRD) Designing pH-shift polymer enzyme pairs to capture CO_2. Contact: Bruce Bunker.
- **Metal-CO_2 adduct formation** (1 year Sandia LDRD), Exploring the potential ability of metals to coordinate and polymerize CO_2, and
- **Thermal diffusion** (1 year Sandia LDRD) Developed the theoretical and design basis for thermal separation of CO_2 from flue gas.
- **Clay separation** (1 year Sandia LDRD) Developed theoretical explanation for CO_2 capture by clay minerals. Contact: Randy T. Cygan.

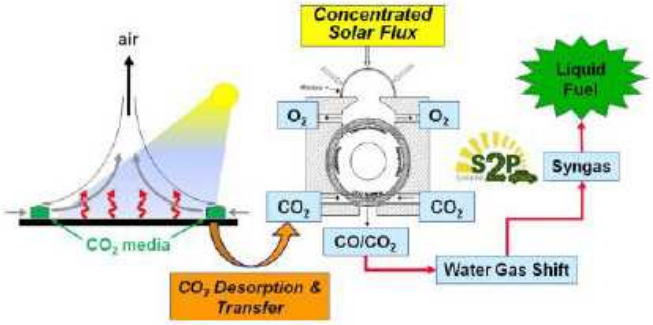


Figure 1. Sunshine to Petrol CO_2 reuse strategy. Contact: Ellen B. Stechel.

Introducing me (worked on too many things, but it comes together)

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Lattice Model for Metal Ammonia Solutions

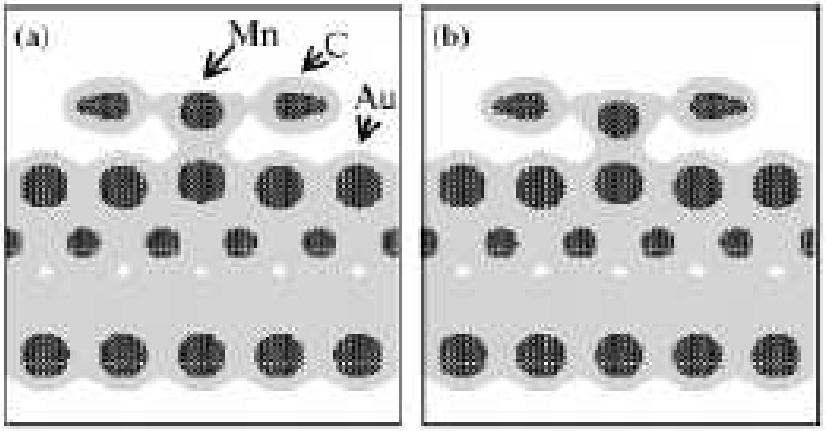
Kevin Leung and Félix S. Csajka
Department of Chemistry, University of California at Berkeley, Berkeley, California 94720
(Received 17 December 1996)

$$S = S' - \sum_{i\sigma}\int_\tau \bar{\psi}_{i\sigma\tau}\Big(\mu_e - \frac{\partial}{\partial\tau} - \phi_i - \lambda_i\Big)\psi_{i\sigma\tau} - t\sum_{\langle ij\rangle\sigma}\int_\tau\Big(1 + \sum_k u_{ik}^{-1}\phi_k\Big)\bar{\psi}_{i\sigma\tau}\psi_{j\sigma\tau}\Big(1 + \sum_l u_{jl}^{-1}\phi_l\Big)$$
$$+ \sum_{ijkl\sigma}\int_\tau \phi_k u_{ki}^{-1}\bar{\psi}_{i\sigma\tau}\psi_{i\sigma\tau}v_{ij}u_{jl}^{-1}\phi_l - \sum_i(\mu_b - 2\Lambda_i - \sigma_i - \xi_i)n_i + \sum_{ijk}\phi_i u_{ij}^{-1}w_{jk}n_k\,. \qquad (4)$$

J|A|C|S
ARTICLES
Published on Web 02/22/2006

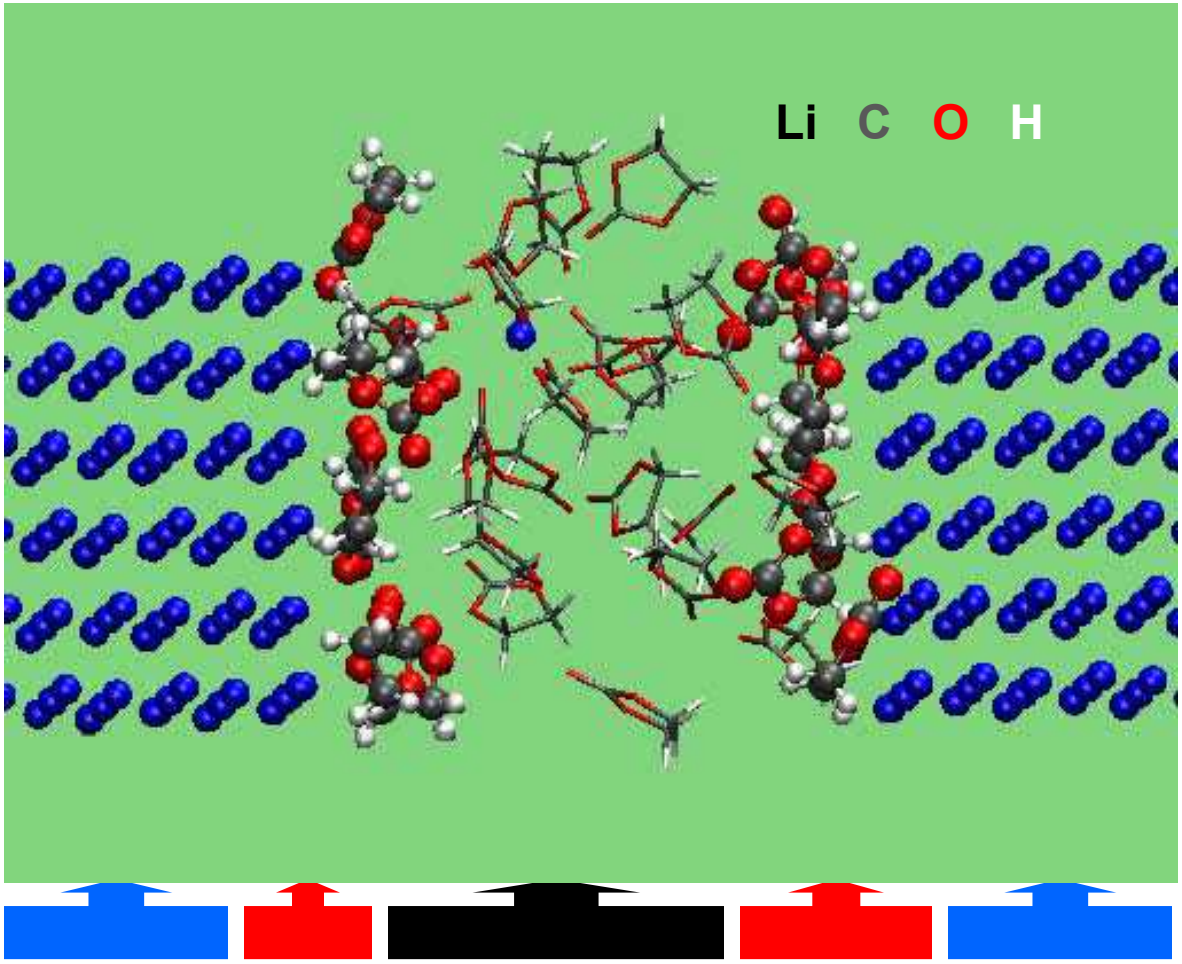
Density Functional Theory and DFT+U Study of Transition Metal Porphines Adsorbed on Au(111) Surfaces and Effects of Applied Electric Fields

Kevin Leung,*,† Susan B. Rempe,† Peter A. Schultz,† Eduardo M. Sproviero,‡ Victor S. Batista,‡ Michael E. Chandross,† and Craig J. Medforth†

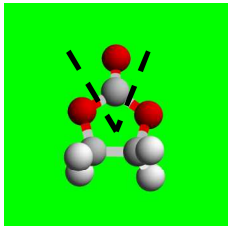


Battery modeling: electrolyte decomposition (SEI)

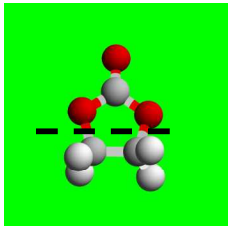
Sacrificial passivation of electrode: electron transfer involved



11/12 EC at the interface decomposes into $OC_2H_4O^{2-}$ + CO, not C_2H_4 + CO_3^{2-}



vs.

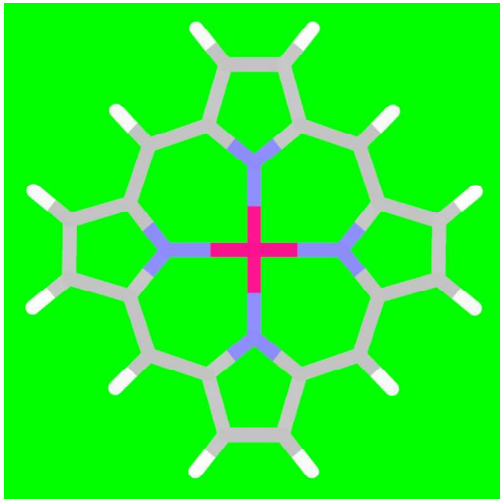


T=350 K

Using *ab initio* molecular dynamics (AIMD)

Recycling CO_2 into transportation fuel

- LBNL's Helios program, S2P at Sandia …..
- CO + H_2 = syn gas, precursor to other hydrocarbons
- Cobalt porphyrin-based catalyst for CO_2 -> CO promising for photo/electrochemical reduction [Furuya & Matsui, J. Electroanal. Chem. (1989)]



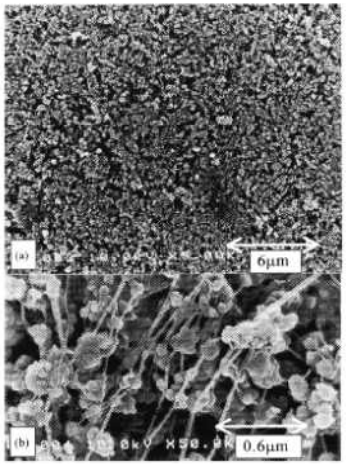
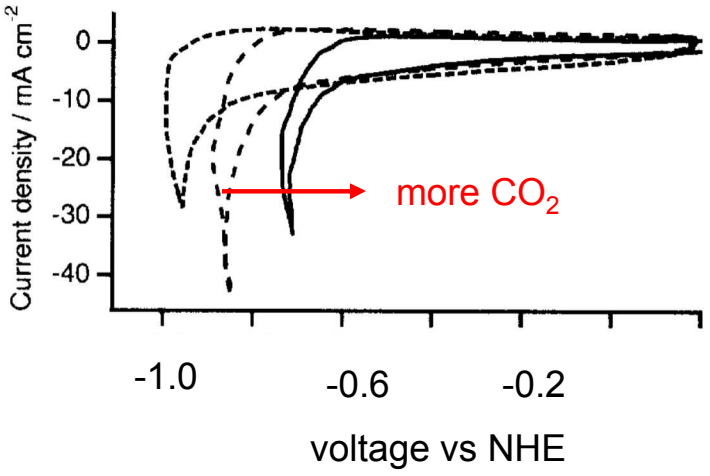


Fig. 1. SEM images of the gas-diffusion electrode. (a) Surface, and (b) cross-section of the reaction layer.

Shibata & Furuya, Electrochim. Acta 48:3953 (2003)



Sonoyama, Kirii, Sakata, Electrochem. Comm. 213 (1999)

- Arakawa et al., Chem. Rev. (2001); Fujita *et al*. (series of ~15 papers)
- Here, first focus on mechanism of electrochemical reduction

Shelnutt's group's experimental work

Ryba, Shelnutt, Prairie, Assink, SAND 97-0414

pH > 7 promotes CO_2 dissolution in water, enhance CO over HCOOH

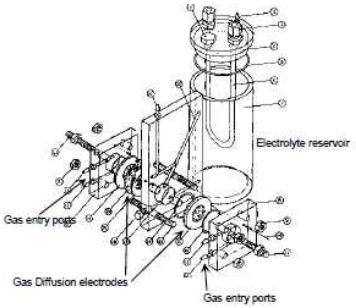
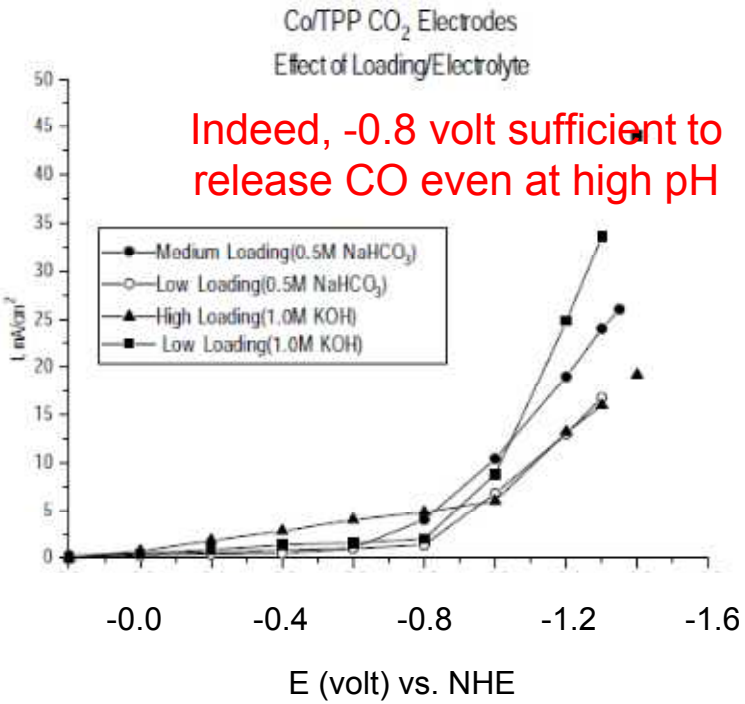


Figure 5 Schematic of ASTRIS Quickcell, taken from product literature. Astris, Inc., 2480 Dunwin Dr., Mississauga, Ontario, Canada L5L 1J9



Indeed, -0.8 volt sufficient to release CO even at high pH

E^0 (Volts vs. NHE)

pH 0		pH 7	pH 14
0.197	Ag/AgCl, KCl (sat'd)	0.197	0.197
+0.169	$CO_{2(g)} + 8H^+ + 8e^- \rightarrow CH_{4(g)} + 2H_2O$	-0.24	-0.65
+0.030	$CO_{2(g)} + 6H^+ + 6e^- \rightarrow CH_3OH_{(aq)} + H_2O$	-0.38	-0.79
0	$2H^+ + 2e^- \rightarrow H_2$	-0.41	-0.82
-0.071	$CO_{2(g)} + 4H^+ + 4e^- \rightarrow HCHO_{(aq)} + H_2O$	-0.48	-0.89
-0.103	CO_2 (g) + 2H+ + 2e- → CO + H_2O	-0.52	-0.93
-0.199	$CO_{2(g)} + 2H^+ + 2e^- \rightarrow HCOOH_{(aq)}$	-0.61	-1.02

Co(I)P/Co(II)P catalyst -0.8 to -0.6 V (NHE) only small overpotential for this reaction

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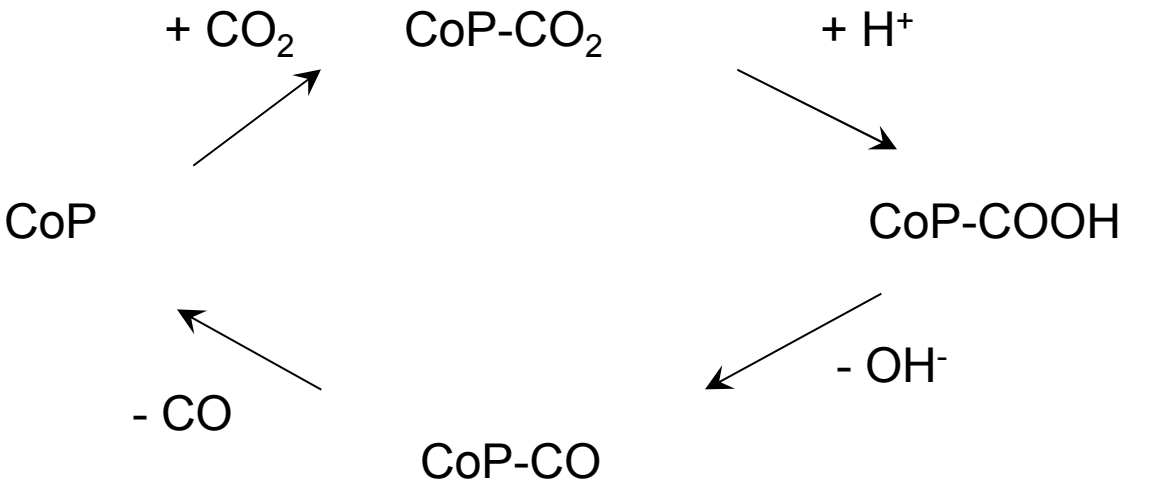
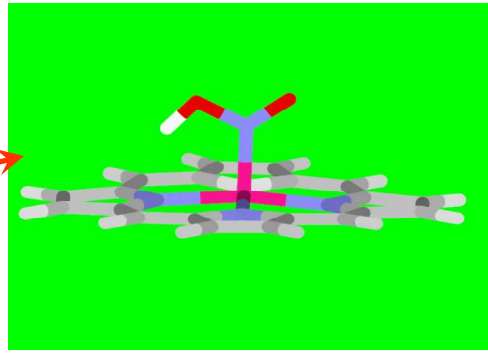
Proposed mechanism, key questions

this multistep, 2-electron reduction reaction in liquid water likely involves:





- how is H^+ added to "-COO^-" at pH > 7?
- when are the 2 electrons added?
- Which is the rate determining step? (or: how do we improve catalyst?)

- Is mechanism viable? (i.e., all steps exothermic?)
- activation barrier consistent with "fast" CO release?

use electronic structure method to answer these question

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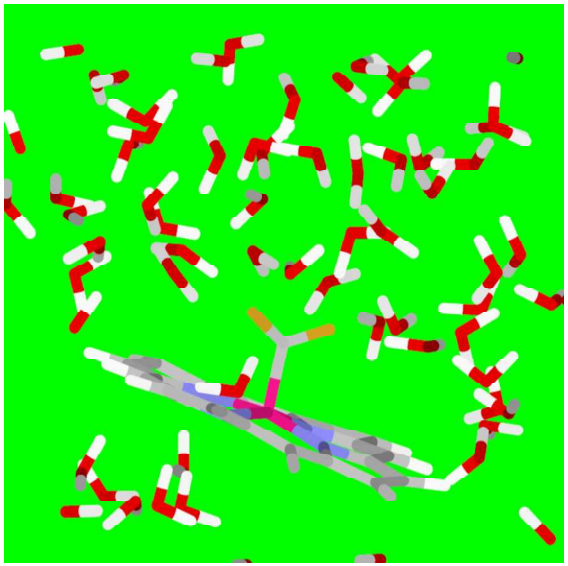
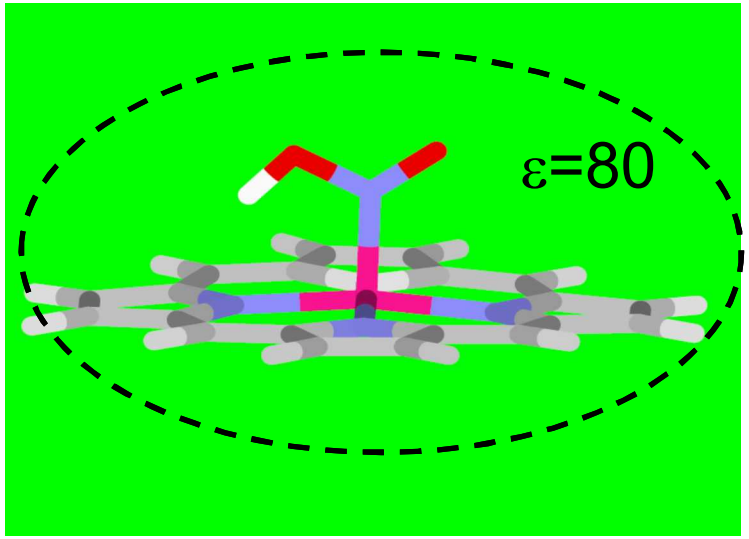
Theoretical methods for this work, in brief

AIMD/DFT+U



- *liquid* water structure, hydrogen bond fluctuations, ion hydration
- rigorous *free energy* predictions via potential of mean force **W(R)**

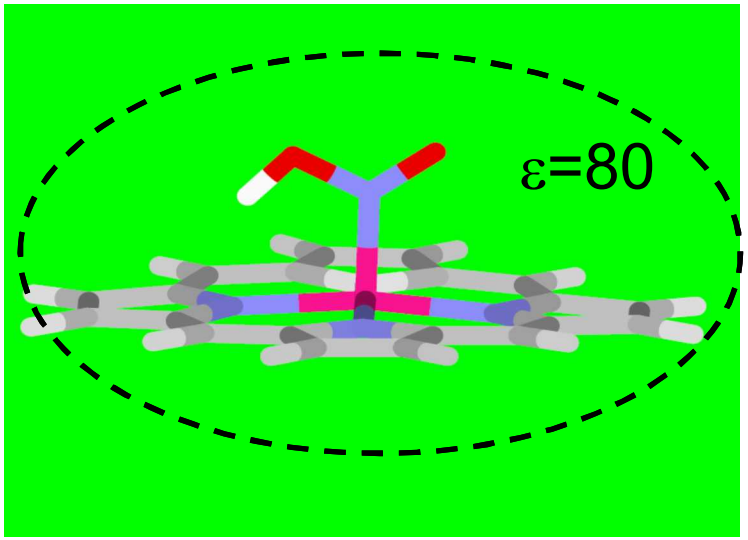
Quantum chemistry/B3LYP



- dielectric solvation
- B3LYP/solvation
- yields redox potential
- New results: M06, explicit water

Gaussian-based Theoretical methods in more detail

- Gaussian suite of codes, B3LYP, other functionals as tests,
- 6-31+G* for geometries, up to 6-311++G(2d,2p) for energies
- PCM dielectric continuum for solvation, ZPE; Nno explicit H_2O
- *This tells us what species (charge states) are important*



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Redox potential from quantum chemistry calculations

Table 1: Mulliken charges and atomic spin densities on the Co atom[a]

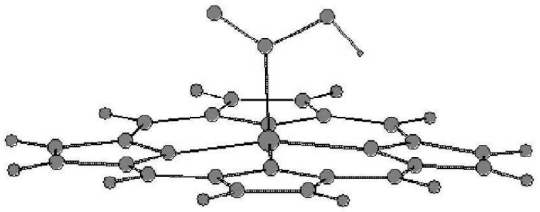
	Charge	Spin
CoP (doublet)	0.96	1.15
CoP (quartet)	0.96	2.76
$[CoP]^+$ (triplet)	1.07	1.91
$[CoP]^+$ (singlet)	1.01	1.16
$[CoP]^-$ (singlet)	−0.07	0.00
$[CoP]^-$ (triplet)	0.16	2.33
$[CoP\text{-}CO]^{+,b}$ (singlet)	0.87	0.00
$[CoP\text{-}CO]^+$ (triplet)	0.88	0.99
$[CoP\text{-}COO]^-$ (singlet)	−0.33	0.00
$[CoP\text{-}COO]^-$ (triplet)	−1.46	2.31
[CoP-COOH] (singlet)	0.80	0.00
[CoP-COOH] (triplet)	0.91	2.35
$[CoP\text{-}COOH]^-$ (doublet)	−0.39	0.00
$[CoP\text{-}COOH]^-$ (quartet)	−1.10	2.78

[a] Computed from the B3LYP wave function using a 6-31G* basis (6-31+G* for anions). For each species, the ground state is listed first. [b] This is a transition state (and is an open-shell singlet with with $\langle S^2 \rangle = 1.05$).

Table 2: Contributions (kcal mol^{-1}) to the total binding energy[a], $\Delta G^{298.15}_{bind}$, for $[CoP\text{–}CO]^+$ in the aqueous phase and in CH_2Cl_2.

	B3LYP		PBE	BP86
	H_2O	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2
$\Delta E^{0,b}_{bind,g}$	10.17	10.17	29.18	27.40
Δ ZPVE[c]	−2.39	−2.39	−2.55	−2.55[g]
$\Delta G^{c,d}_{thermal}$	−10.79	−10.79	−10.61	−10.61[g]
ΔG^{e}_{solv}	−3.83	−4.37	−1.69	− 2.22
Standard state conversion[f]	+1.89	+1.89	+1.89	+ 1.89
$\Delta G^{298.15}_{bind}$	−4.95	−5.49	16.22	13.91

[a] Using a 1 M reference state both in solution and in the gas phase.
[b] 6-311++G(2d,2p) value at 0 K in the gas phase.
[c] 6-31G* value in the gas phase.
[d] Computed as $\Delta G^{298.15}_{bind,g.} - \Delta G^{0}_{bind,g.}$
[e] 6-311++G(2d,2p) value computed in H_2O or CH_2Cl_2.
[f] Conversion from 1 atm to 1 M standard state in the gas phase.
[g] Using the PBE value.



CoPCOOH$^-$: H-bond to N atom

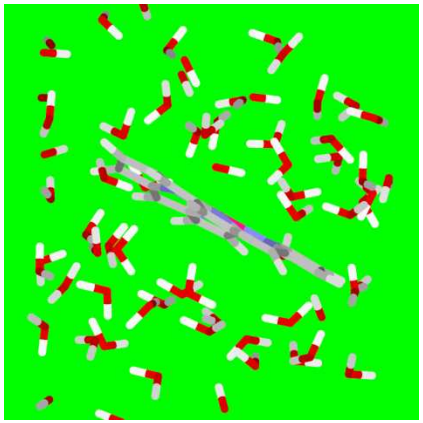
Table 3: Reaction energies (kcal mol^{-1}) for proposed steps in the reduction of CO_2 by cobalt porphyrins; reduction potentials (eV) given in parentheses. After each porphyrin species the spin multiplicity is given in parentheses, with 1=singlet, 2=doublet, etc.[a]

Eq.		$\Delta G^{298.15}_{aq.}$ B3LYP	ΔE^{0}_{g} B3LYP	ΔE^{0}_{g} PBE	ΔE^{0}_{g} BP86
(2)	$[CoP]^-(1) + CO_2 \rightarrow [CoP\text{–}CO_2]^-(1)$	7.63	0.38	−3.73	−1.70
(3)	$[CoP\text{–}CO_2]^-(1) + H^+ \rightarrow CoP\text{–}COOH(1)$	−10.39	−327.71	−321.57	−322.42
(4)	$CoP\text{–}COOH(1) + e^- \rightarrow [CoP\text{–}COOH]^-(2)$	−75.30 (1.17)	−30.32	−8.10	−9.92
(5)	$[CoP\text{–}COOH]^-(2) + H^+ \rightarrow CoP(2) + CO + H_2O$	−48.69	−338.88	−329.39	−335.30
(6)	$[CoP\text{–}COOH]^-(2) + H^+ \rightarrow CoP(2) + HCOOH$	−56.17	−352.06	−349.58	−352.98
(7)	$CoP\text{–}COOH(1) + H^+ \rightarrow [CoP\text{–}CO]^+(1) + H_2O$	5.10	−221.19	−218.01	−221.75
(8)	$[CoP\text{–}CO]^+(1) + e^- \rightarrow CoP(2) + CO$	−129.09 (−1.16)	−148.01	−119.48	−123.46
(9)	$CoP(2) + e^- \rightarrow [CoP]^-(1)$	−63.02 (1.71)	−24.73	−43.46	−45.48
(10)	$[CoP\text{–}CO]^+(1) \rightarrow [CoP]^+(3) + CO$	−5.19	11.74	30.48	28.77

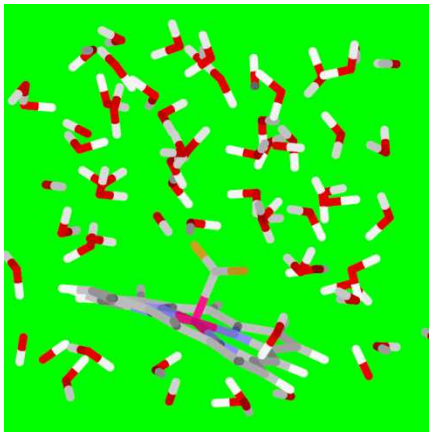
redox potentials vs NHE: B3LYP
$[Co(0)P]^-/[Co(I)P]^-$ -2.1 volt
$[Co(I)P]^-/Co(II)P$: -1.7 volt
$Co(II)PCOOH^-/Co(II)PCOOH$: -1.2 volt
$Co(II)PCOOH^{2-}/Co(II)PCOOH^-$:-2.0 volt
$Co(I)PCO_2^{2-}/Co(I)PCO_2^-$: -1.7 volt

Hydrogen bonding in water stabilizes some products (AIMD snapshots)

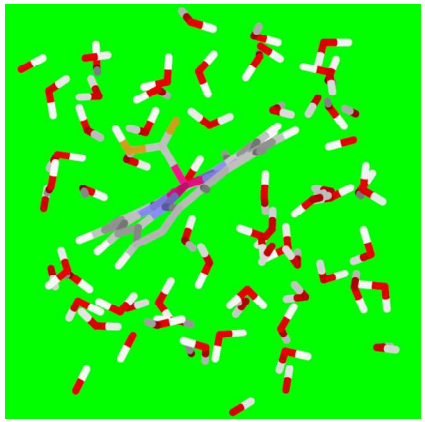
CoP $\xrightarrow{+ CO_2}$ $CoPCO_2$ $\xrightarrow{+ H^+}$ CoPCOOH



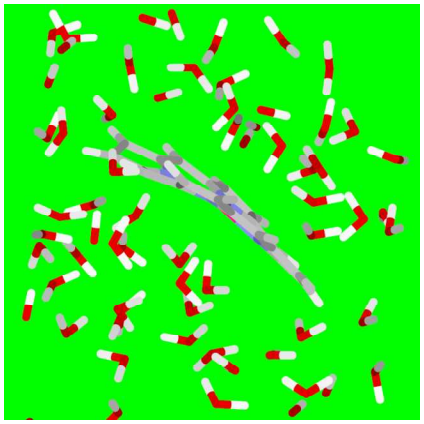
$Co(I)P^-$



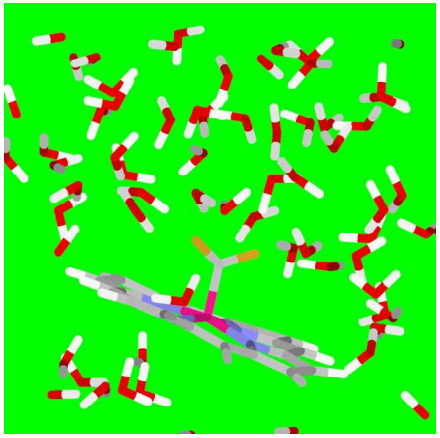
$Co(I)PCO_2^-$



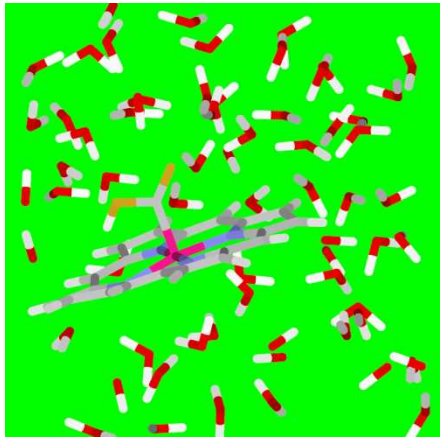
Co(II)PCOOH



$Co(I)P^{2-}$

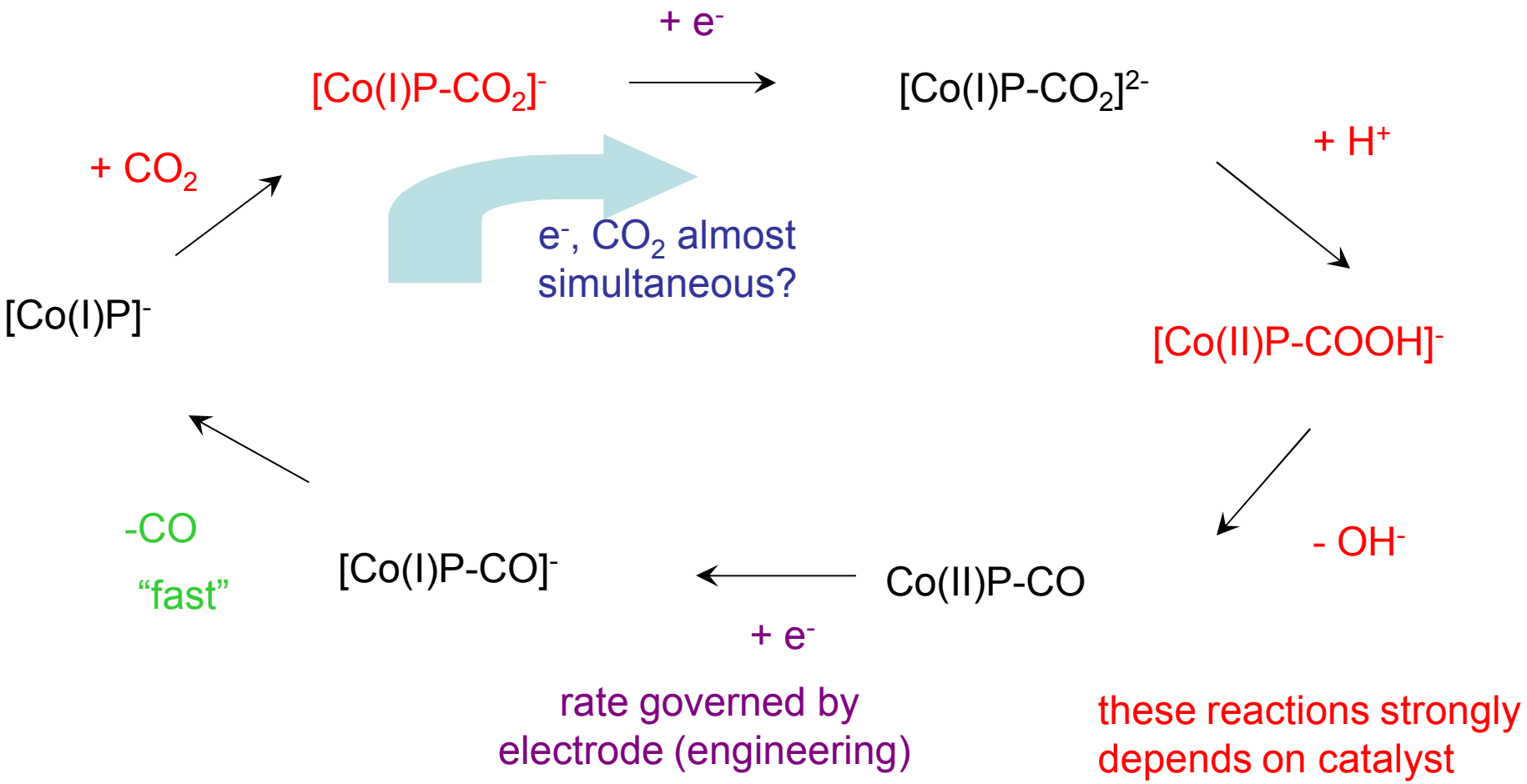


$Co(I)PCO_2^{2-}$



$Co(II)PCOOH^-$

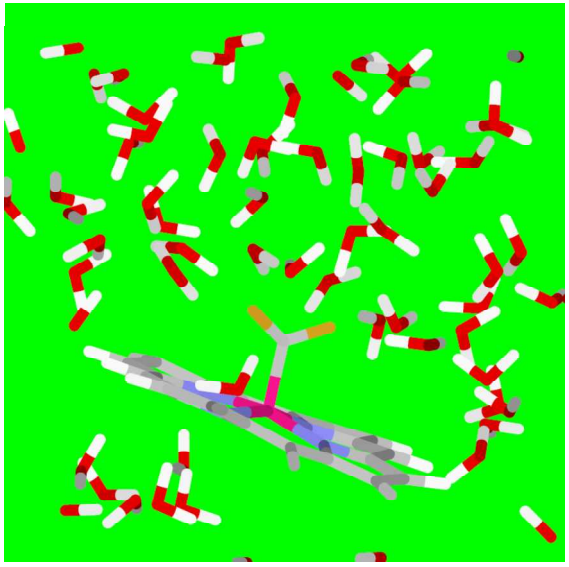
Proposed mechanism (including e^-)



next use AIMD to interrogate 3 key details of $[CoP\text{-}COOH]^-$ reactions

AIMD Theoretical methods in more detail

- *ab initio* molecular dynamics (AIMD): "chemical reactions in real time"
- based on DFT, VASP code, PBE functional, T=425 K
- $(13.6\ A)^3$, 71 H_2O, BO dynamics, 0.25 fs time step, 10^{-6} eV convergence …
- DFT+U treatment of Co ion, U=2.5 eV
- Umbrella sampling technique



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DFT accuracy: calibration with experiments

- Co(III)P + CO -> $[Co(III)P\text{-}CO]^+$ (in CH_2Cl_2):

Expt : ΔG = -5.9 kcal/mol [Mu & Kadish, Inorg. Chem. 28:3743 (1989)]

PBE : ΔG = -16.2 kcal/mol

B3LYP: ΔG = +5.2 kcal/mol

popular functionals: O(1) eV errors for 3-d metal complexes/oxides

Calibrate VASP/DFT+U: U = 2.5 eV, ΔG ~ -5.9 (see later)

Other semi-local DFT methods for 3-d metal ions

- Self consistent DFT+U
  [Cococcioni & de Gironcoli, PRB 71:035105 (2005)]
- Quasi-self-interaction corrections
  [Stengel & Spaldin, PRB 77:155106 (2007)]
- New functionals
  [Zhao & Truhlar, JCP 125:194101 (2006)]
- Gutzwiller DFT ("DFT+G")
  [Wang, Dai, Fang, PRL 101:066403 (2008)]

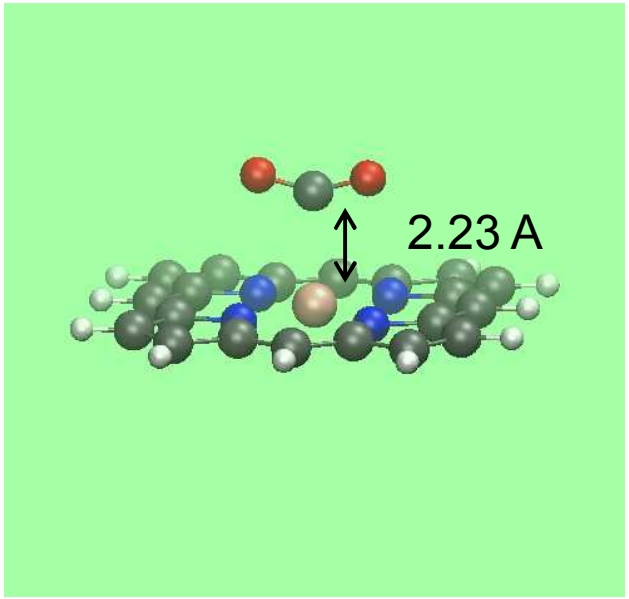
$Co(I)P\text{-}CO_2$ binding (free) energy, gas vs aqueous

(New, unpublished)

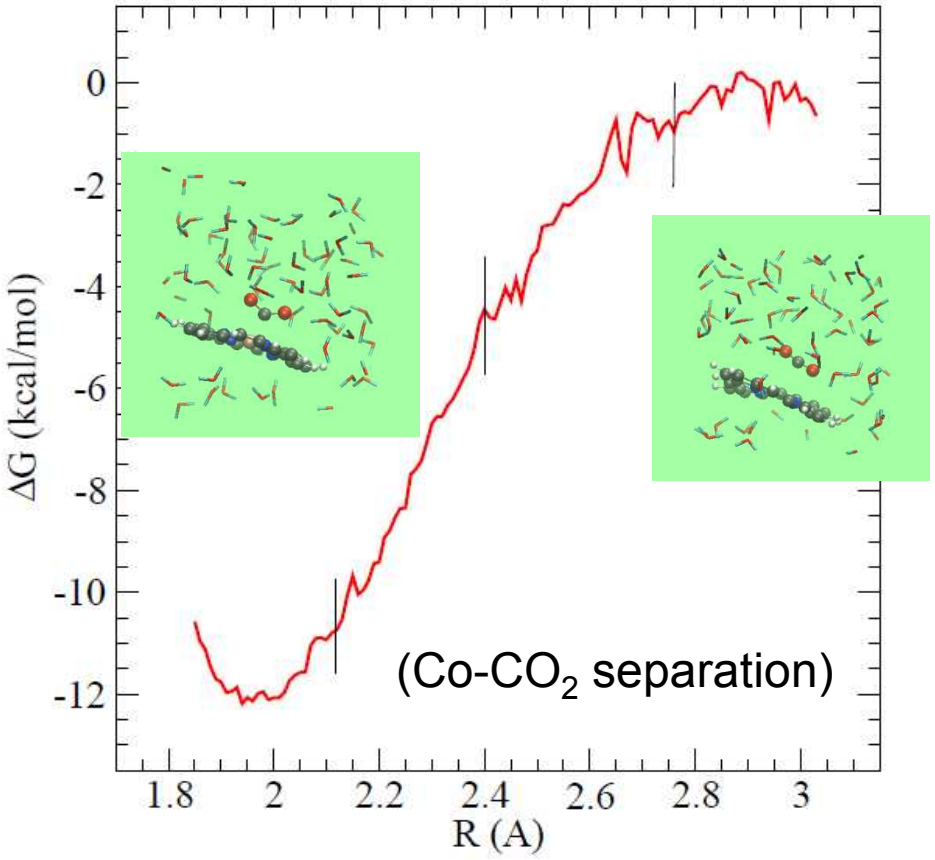
gas phase binding energy at

T=0 K: 0.12 eV (2.7 kcal/mol)

-- unbound if entropy added



aqueous state AIMD: stronger binding



$Co(I)P\text{-}CO_2$ stable in water; formation of complex is barrierless

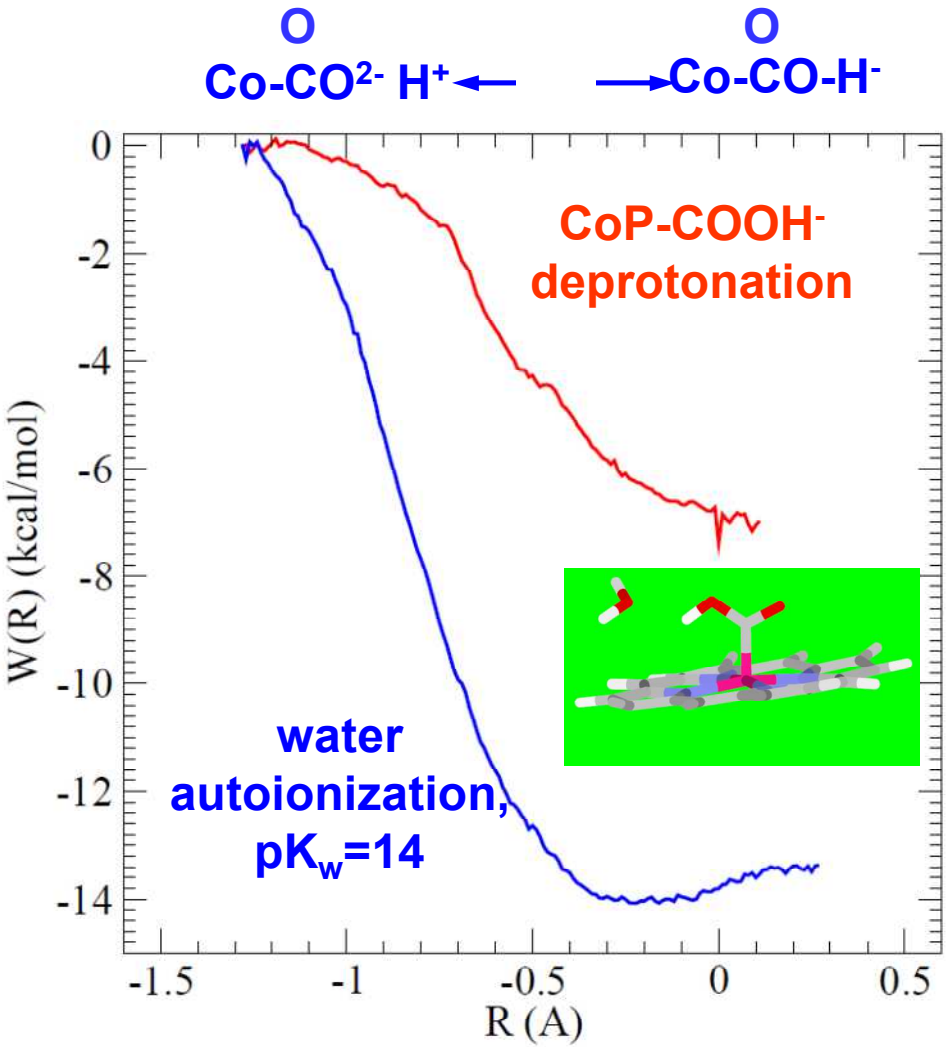
AIMD: acidity of $[CoPCOOH]^-$ (aq)

new 4-atom reaction coordinates [Leung, Nielsen,Criscenti (2009)]

$[CoPCOOH]^- \rightarrow [CoPCO_2]^{2-} + H^+$

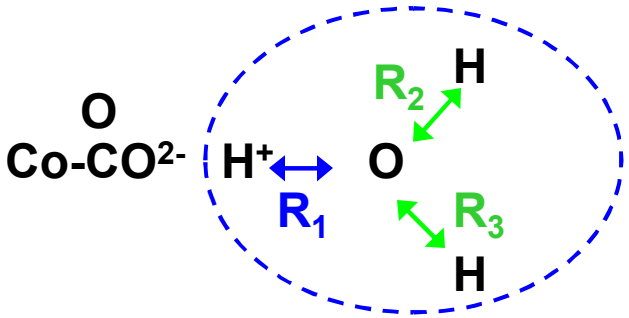
$\Delta G - \Delta G_{water} \sim 7$ kcal/mol; $pK_a \sim 9$

- $[CoPCOOH]^-$ not very acidic (unlike CoPCOOH or HCOOH)
- reaction should proceed at pH >7

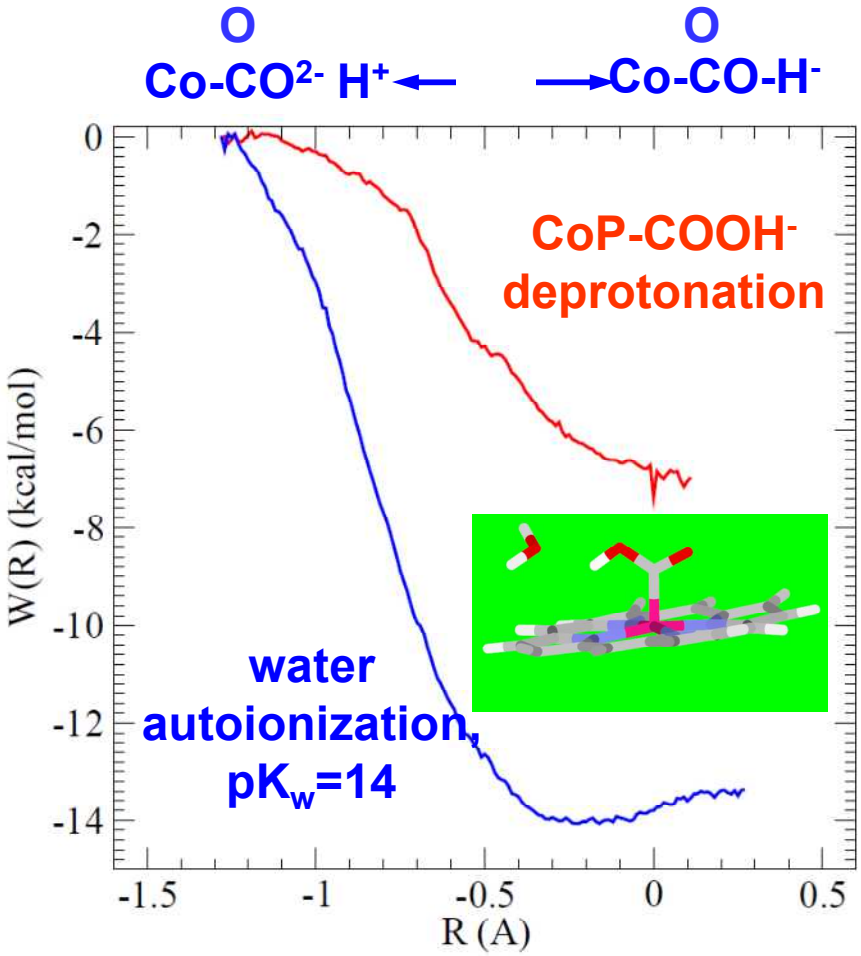


[CoPCOOH]$^-$ (aq) deprotonation reaction coordinate

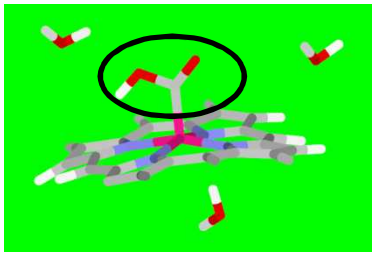
- new reaction coordinates
  [Leung, Nielsen,Criscenti (2009)]



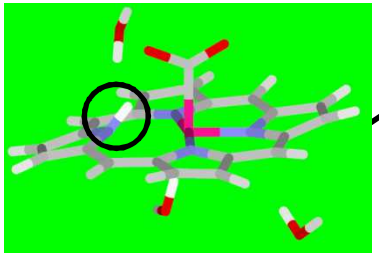
$R = R_1 - R_2 - R_3$



AIMD: C-OH bond breaking barrier in water

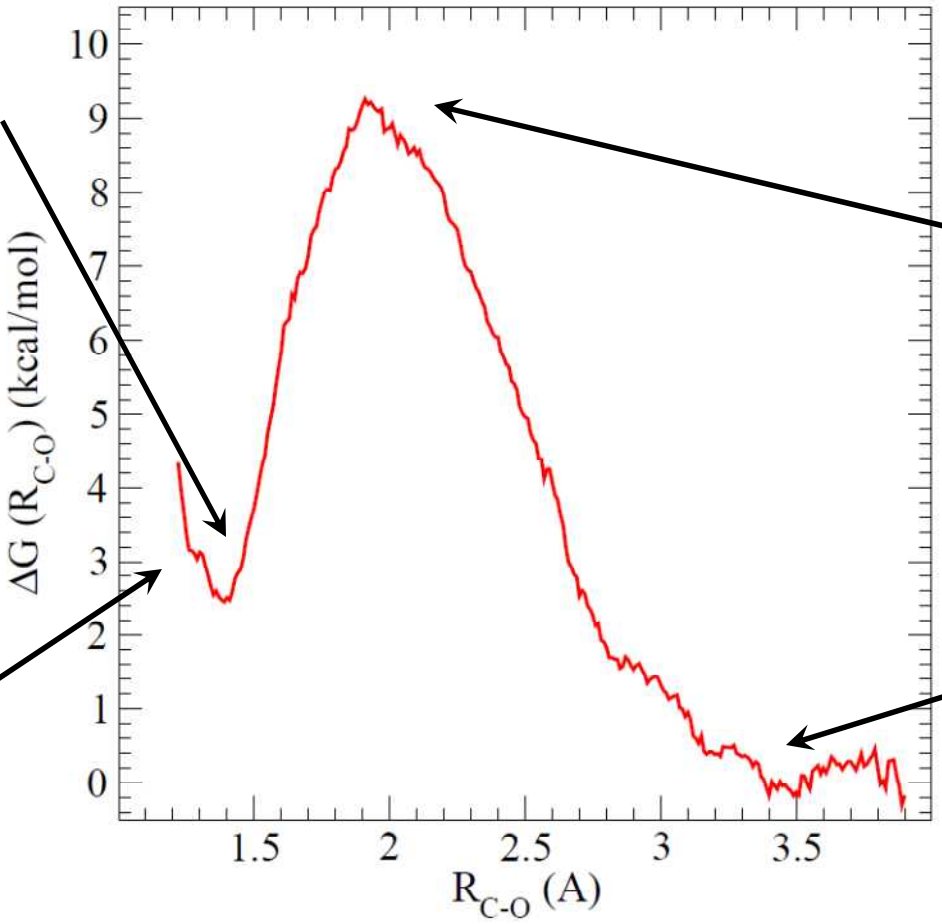


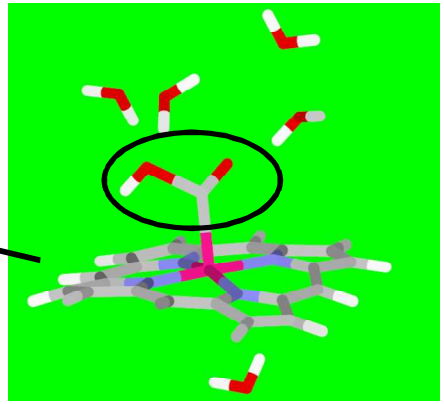
CoP-COOH$^-$



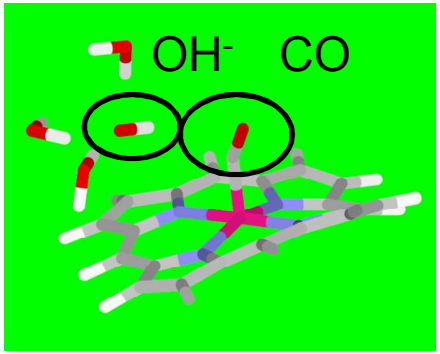
-NH$^+$ motif

[-C-OH]$^-$ ← → -C + OH$^-$





C-O bond
almost broken

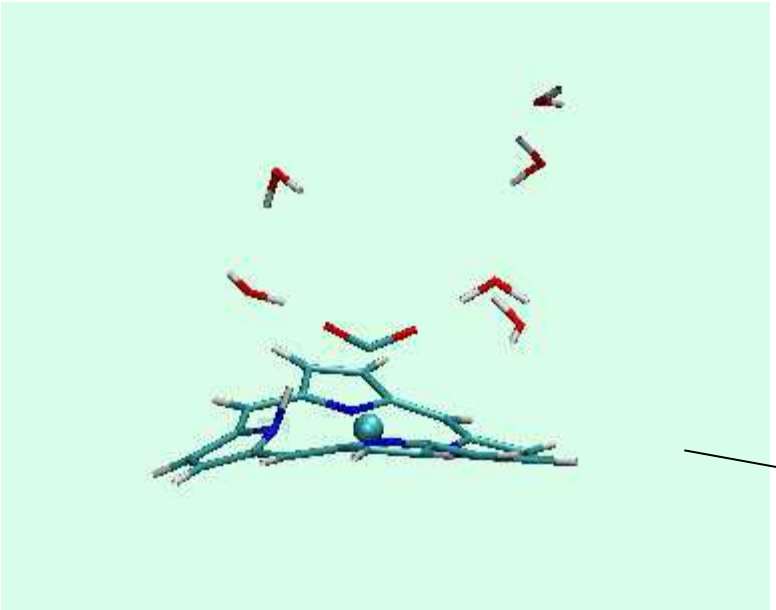


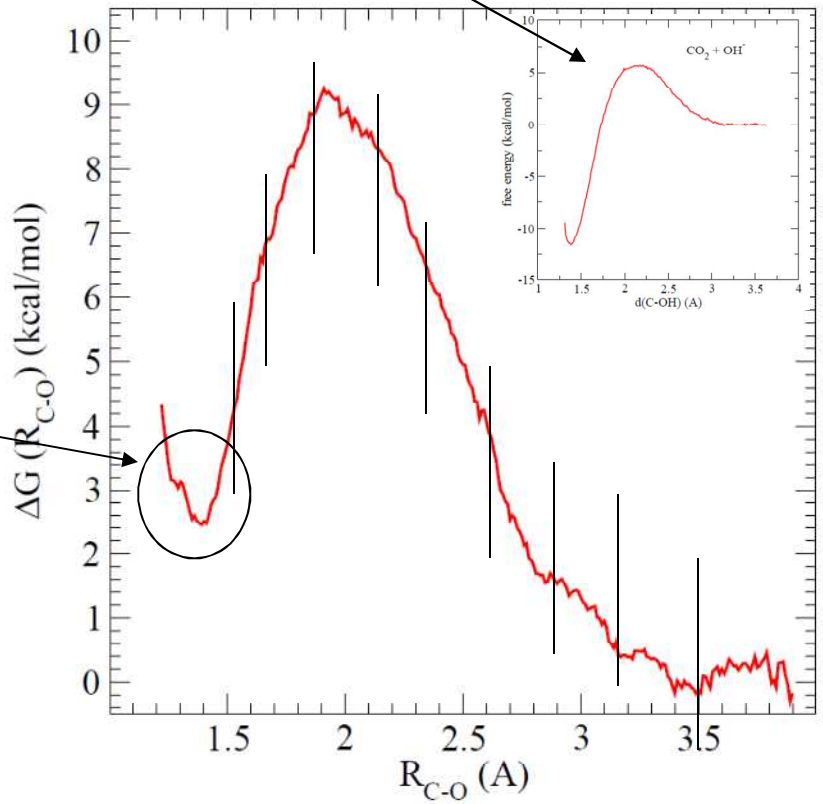
CoP-CO + OH$^-$

C-OH cleavage barrier

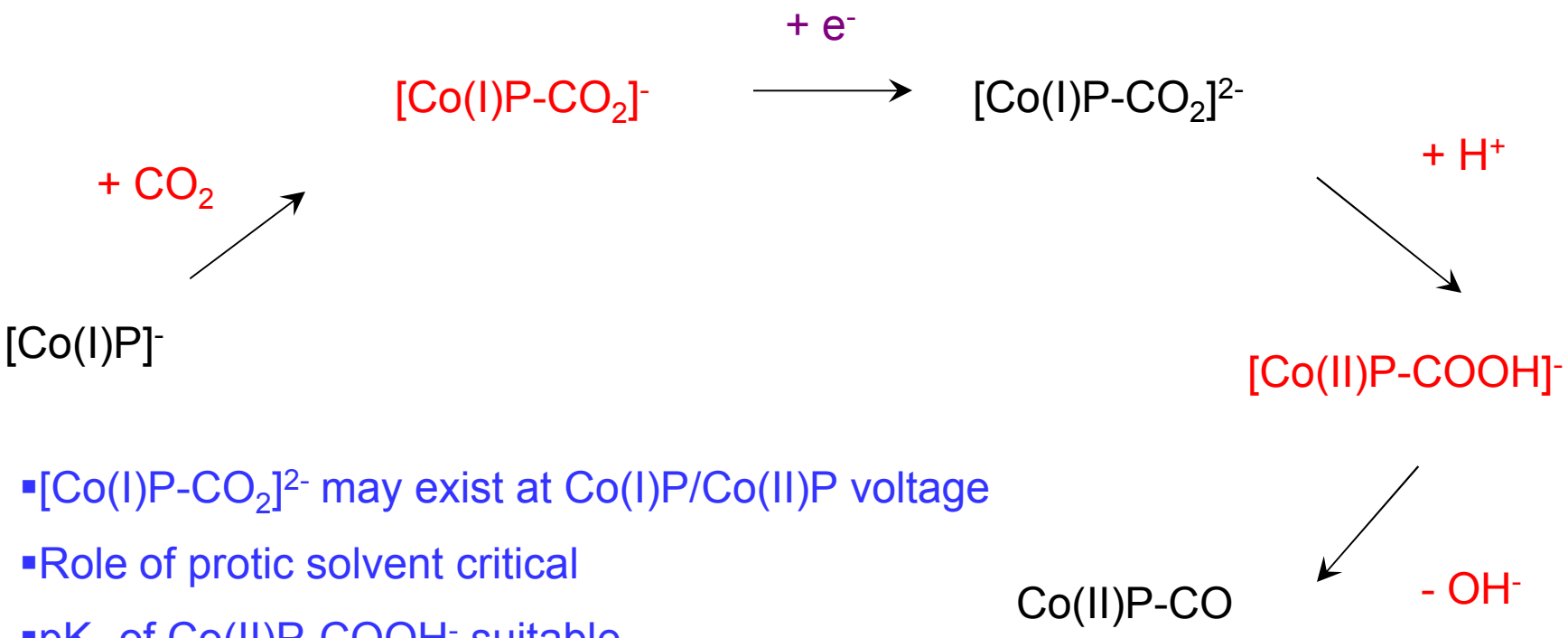
$[CoPCOOH]^- \rightarrow [CoPCO] + OH^-$ $\Delta G^* \sim 5.2$ kcal/mol

$CO_3H^- \rightarrow CO_2 + OH^-$ [Leung, Nielsen, Kurtz JPCB (2007)] $\Delta G^* \sim 18.5$ kcal/mol





Insight about reaction mechanism



- $[Co(I)P\text{-}CO_2]^{2-}$ may exist at Co(I)P/Co(II)P voltage
- Role of protic solvent critical
- pK_a of $Co(II)P\text{-}COOH^-$ suitable
- $C\text{-}OH^-$ cleavage barrier reasonable

Revisit redox potential with M06 calculations

redox potentials vs NHE:	B3LYP (old)	M06 (new)
$[Co(I)P]^-/Co(II)P$ $[Co(0)P]^-/[Co(I)P]^-$	-1.7 V (expt: -0.9 V) -2.1 V	-1.6 -1.8
$Co(II)PCOOH^-/Co(II)PCOOH$	-1.2 V	NA
$Co(II)PCOOH^{2-}/Co(II)PCOOH^-$	-2.0 V	NA
$Co(I)PCO_2^{2-}/Co(I)PCO_2^-$	-1.7 V	-1.8
$Co(I)PCO_2^-/Co(I)PCO_z$	-1.2 V	-1.1

M06: 6-311+G(d,p)/6-31+G* with “smd” dielectric

Not much improvement – need less % exchange in DFT functional

New slide – redox potential in liquid
Everything is faster

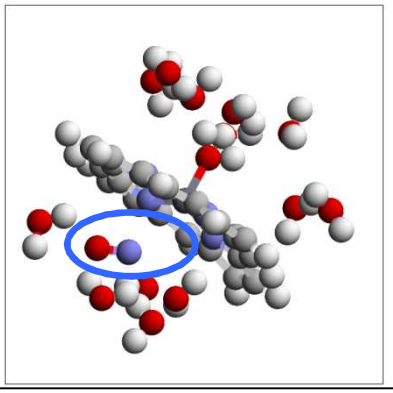
Conclusions and Outlook

- now understand why reaction works at pH ~ 9
- Co catalyzed C-OH cleavage barrier in $CoPCOOH^-$ is reasonable
- $CoPCOOH^-$ is likely the key intermediate

- electron transfer rate not yet calculated – could be rate-determining!
- more accurate electronic structure methods need to be found

Challenges of modeling photo/electrochemistry

Leung, Medforth J. Chem. Phys.(2007)

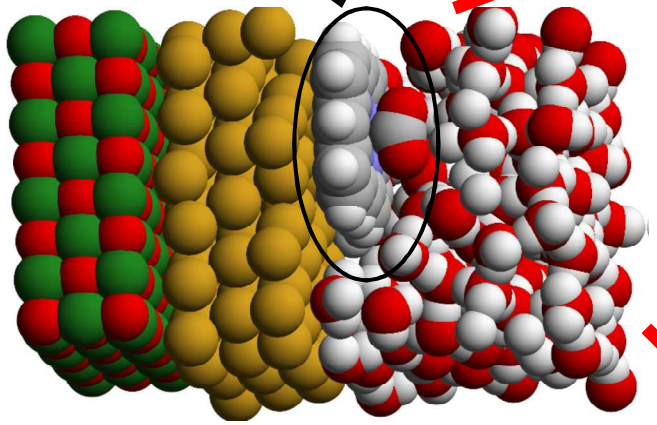


B3LYP and PBE both inaccurate for Mn(III)P-NO complex

bond-breaking: DFT accuracy

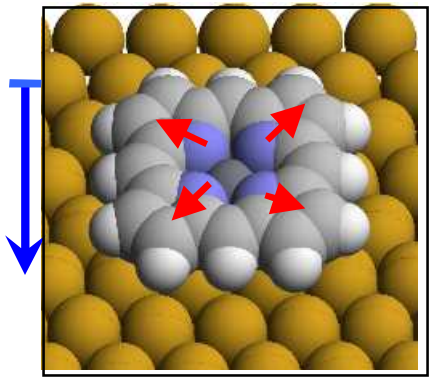
excited state properties

$Co(I)P\text{-}CO_2 + 2OH^- \rightarrow Co(III)P\text{-}CO + H_2O$



water

Leung, Rempe, Schultz, … Medforth, JACS (2006), **using DFT+U**



Electrode-electrolyte interface

constant voltage calculation

electron transfer rate (Marcus theory)

electronic structure calculations, especially those with explicit solvent difficult to run in “constant voltage” mode

Use AIMD to calculate redox potentials

$\Phi = \Delta G_{hyd}$ + (ionization potential differences)

THE JOURNAL OF CHEMICAL PHYSICS **130**, 204507 (2009)

Ab initio molecular dynamics calculations of ion hydration free energies

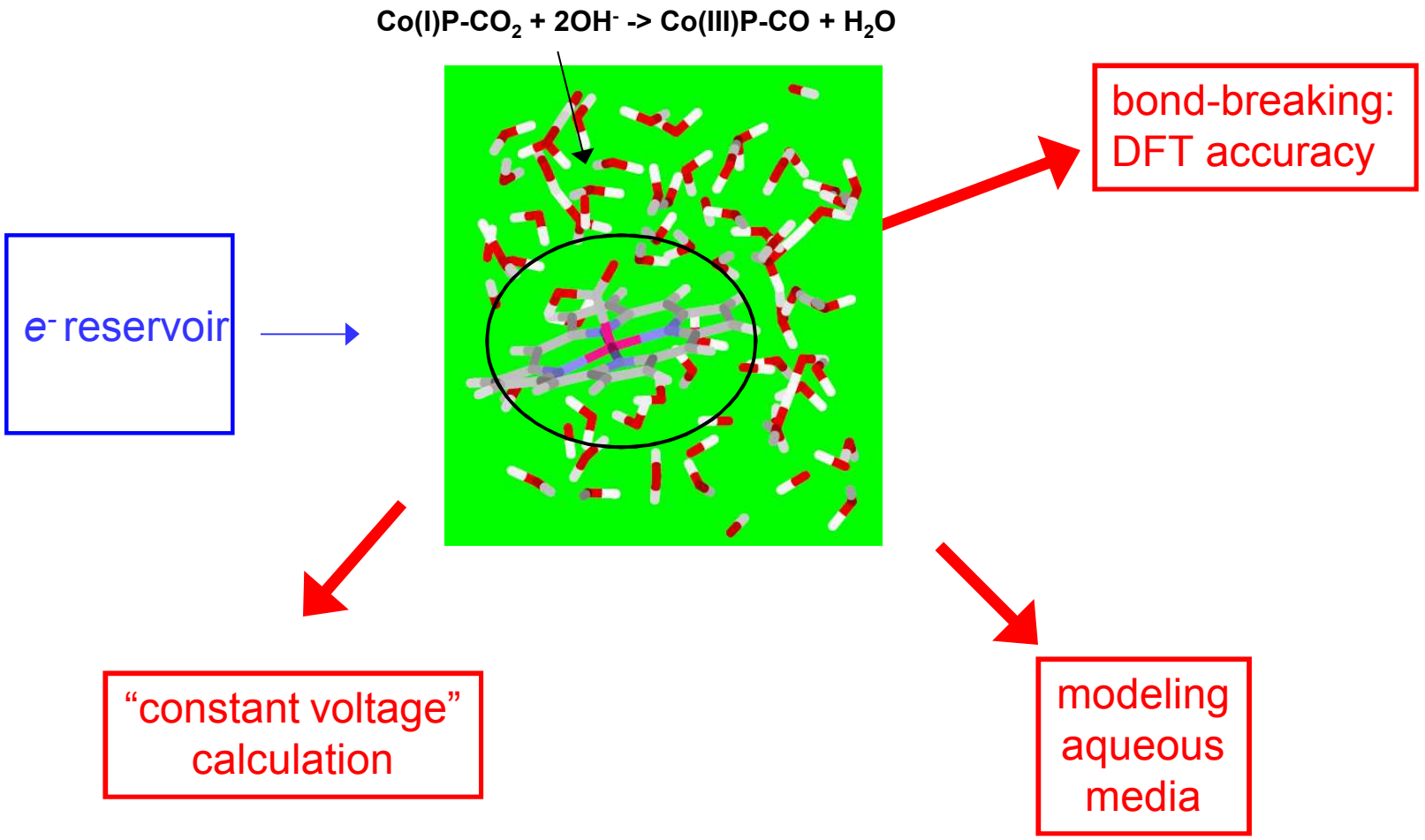
Kevin Leung,[1,a)] Susan B. Rempe,[2] and O. Anatole von Lilienfeld[3]

$$\Delta G_{hyd} = \int_0^1 d\lambda \left\langle \frac{dH(\lambda)}{d\lambda} \right\rangle_\lambda$$

Ion	N_{water}	ρ_{water}	Quadrature	ΔG_{hyd}
Li^+	32	1.00	2-pt	−128.6
Li^+	32	1.00	6-pt	−128.3
Li^+	64	1.00	2-pt	−126.7
Li^+	32	0.97	2-pt	−126.7
Li^+	32	0.97	6-pt	−127.2
Li^+	SPC/E	1.00	6-pt	−134.9
Li^+	Expt.[a]	1.00	NA	−113.5
Li^+	Expt.[a,†]	1.00	NA	−137.0
Li^+	Expt.[b]	1.00	NA	−126.5
Li^+	Expt.[b,†]	1.00	NA	−133.2

Ion	N_{water}	ρ_{water}	Quadrature	ΔG_{hyd}
Cl^-	32	1.00	2-pt	−79.0
Cl^-	32	1.00	6-pt	−76.6
Cl^-	32*	1.00	6-pt	−69.3
Cl^-	32 SPC/E	1.00	2-pt	−71.0
Cl^-	256 SPC/E	1.00	2-pt	−67.7
Cl^-	Expt.[a]	1.00	NA	−81.2
Cl^-	Expt.[a,†]	1.00	NA	−65.3
Cl^-	Expt.[b]	1.00	NA	−72.6
Cl^-	Expt.[b,†]	1.00	NA	−69.7
Li^+/Cl^-	32	1.00	6-pt	−197.6
Li^+/Cl^-	SPC/E	1.00	2-pt	−202.6
Li^+/Cl^-	Expt.[a]	1.00	NA	−202.3
Li^+/Cl^-	Expt.[b]	1.00	NA	−202.9

Computation electrochemistry in our case



- Experimental electrochemistry: 200+ years
- Computational electrochemistry: very hot topic

Calculating the redox state (determined by system)

(can only add electrons to simulation cell, not put electron on Co)

- Need to know redox state reliably
- Heather's d-orbital Hartree matrix
- Wannier decomposition (U=2.5eV)
- Experimental: Co(II)TPP -> Co(I)TPP -> Co(I)[TPP^{-}], same for OEP?
- PBE mistake in macrocycle orbital levels (blue boxes)? check with B3LYP!

$[CoP]^{+}$	$[CoPCO]^{+}$	$[CoPCOOH]$	$[CoPCOOH]$ (aq)
Co(III) s=1	Co(III) s=0	Co(III) s=0	Co(III) s=0
$[CoP]$	$[CoPCO]$	$[CoPCOOH]^{-}$	$[CoPCOOH]^{-}$ (aq)
Co(II) s=1/2	Co(II) s=1/2	Co(III) s=0	Co(II) s=1/2
$[CoP]^{-}$	$[CoPCO]^{-}$	$[CoPCOOH]^{2-}$	$[CoPCOOH]^{2-}$ (aq)
Co(II) s=1/2 or Co(I) s=0	Co(I) s=1	Co(II) s=1/2 or Co(III) s=0	Co(II) s=3/2?

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