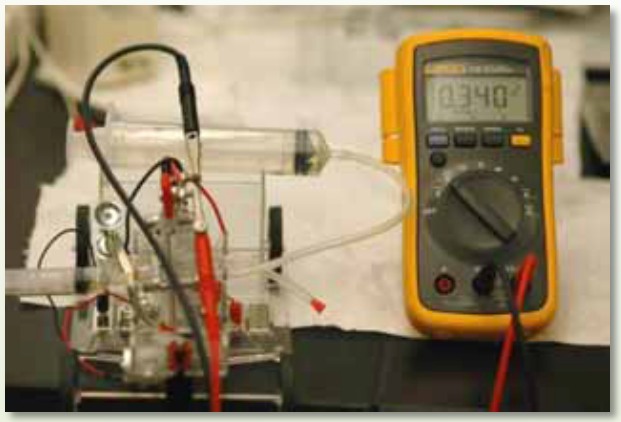


CHEM 505: *Green Chemistry and Alternative Energy*

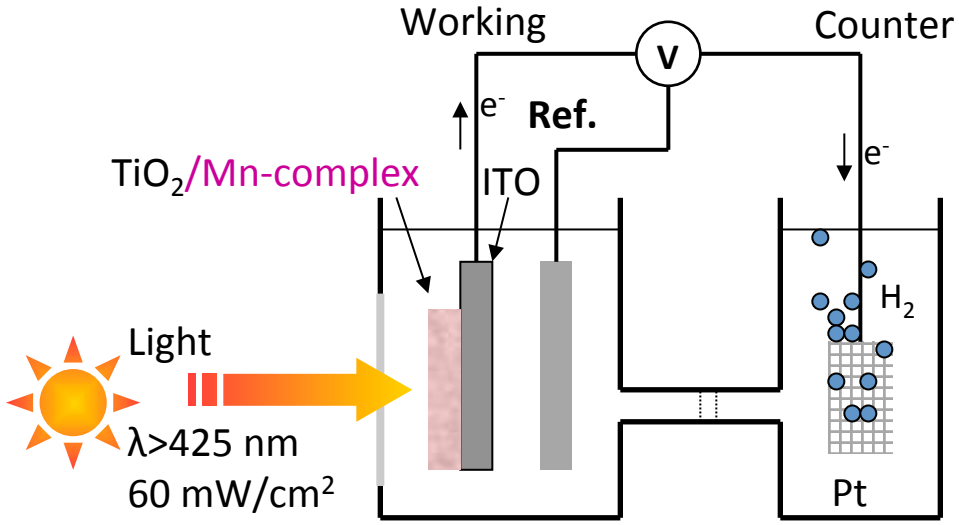
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

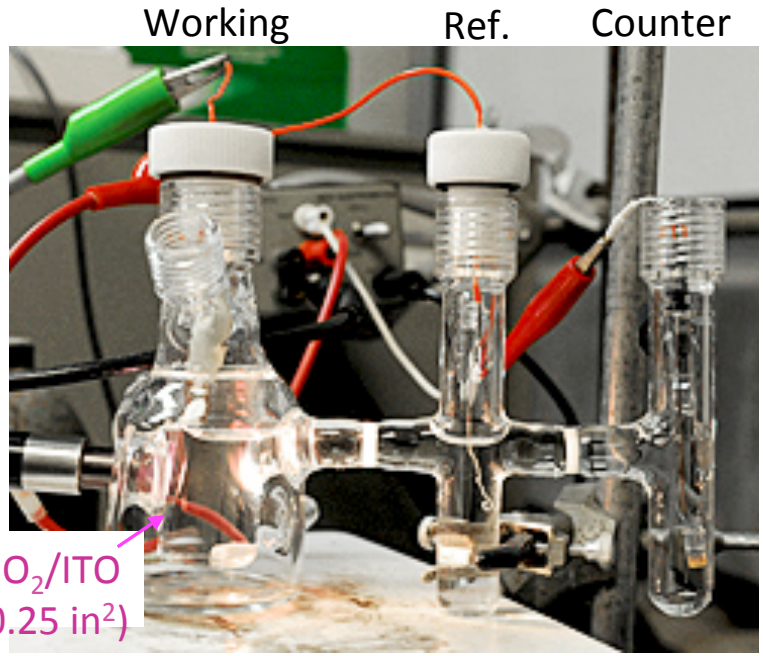
Modeling Systems for a Hydrogen Economy

Photocatalysis with Visible Light

Dr. Gonghu Li
Dr. Christiaan Richter

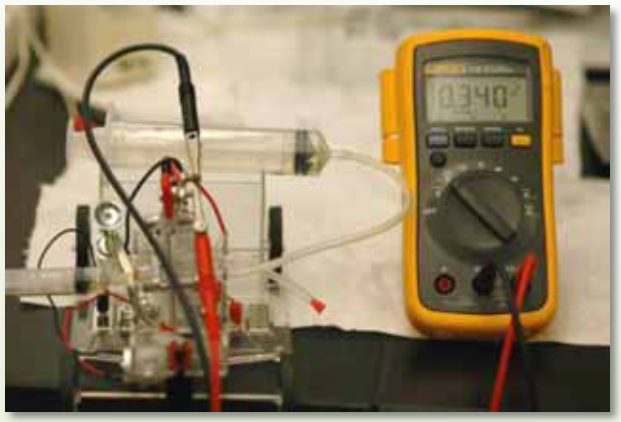
Photooxidation of isopropanol





$(CH_3)_2CHOH \longrightarrow (CH_3)_2C{=}O + 2H^+ + 2e^-$

$2H^+ + 2e^- \longrightarrow H_2$



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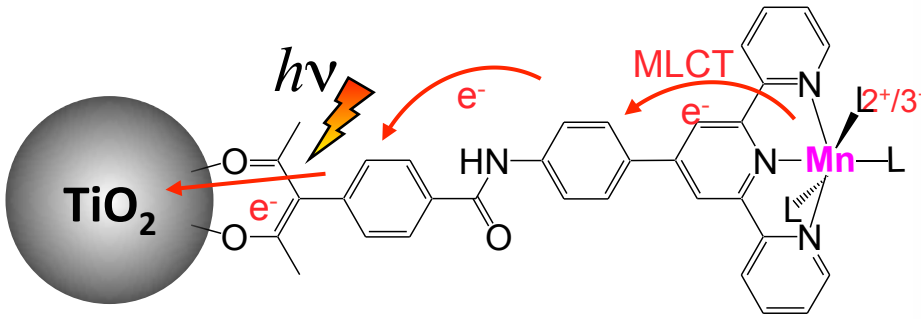
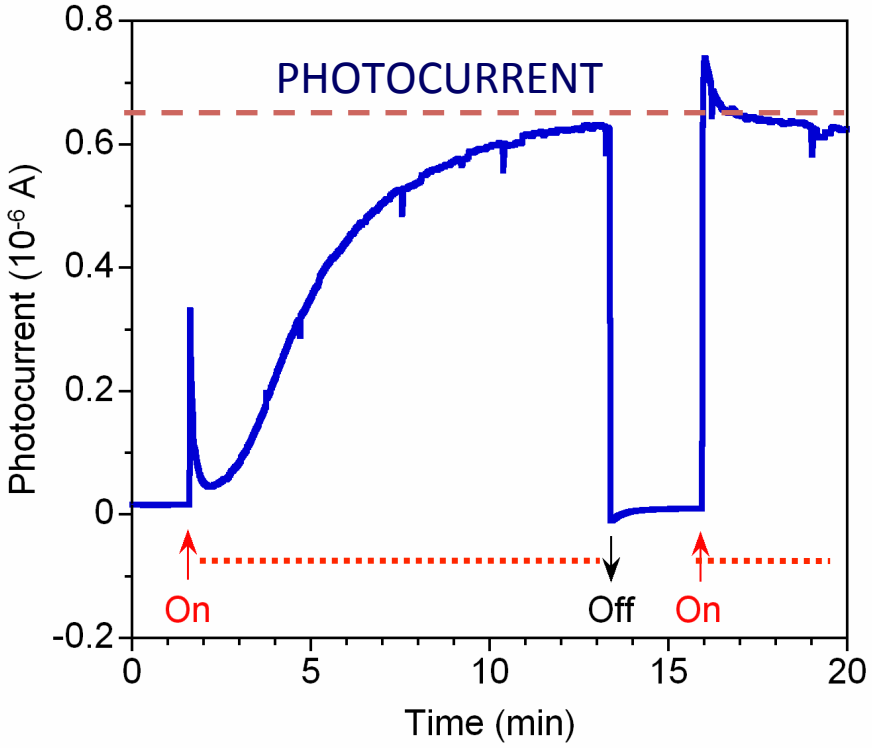
Photooxidation of isopropanol

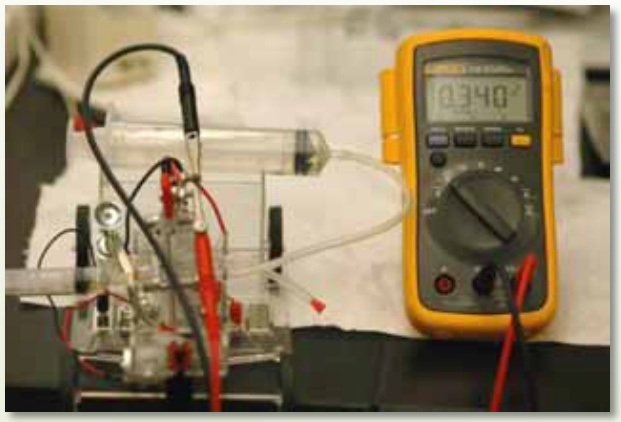
Net redox reaction:

$$(CH_3)_2CHOH \xrightarrow[TiO_2/Mn\text{-}cat.]{h\nu} (CH_3)_2C{=}O + H_2$$

Photoactivation of the catalyst:

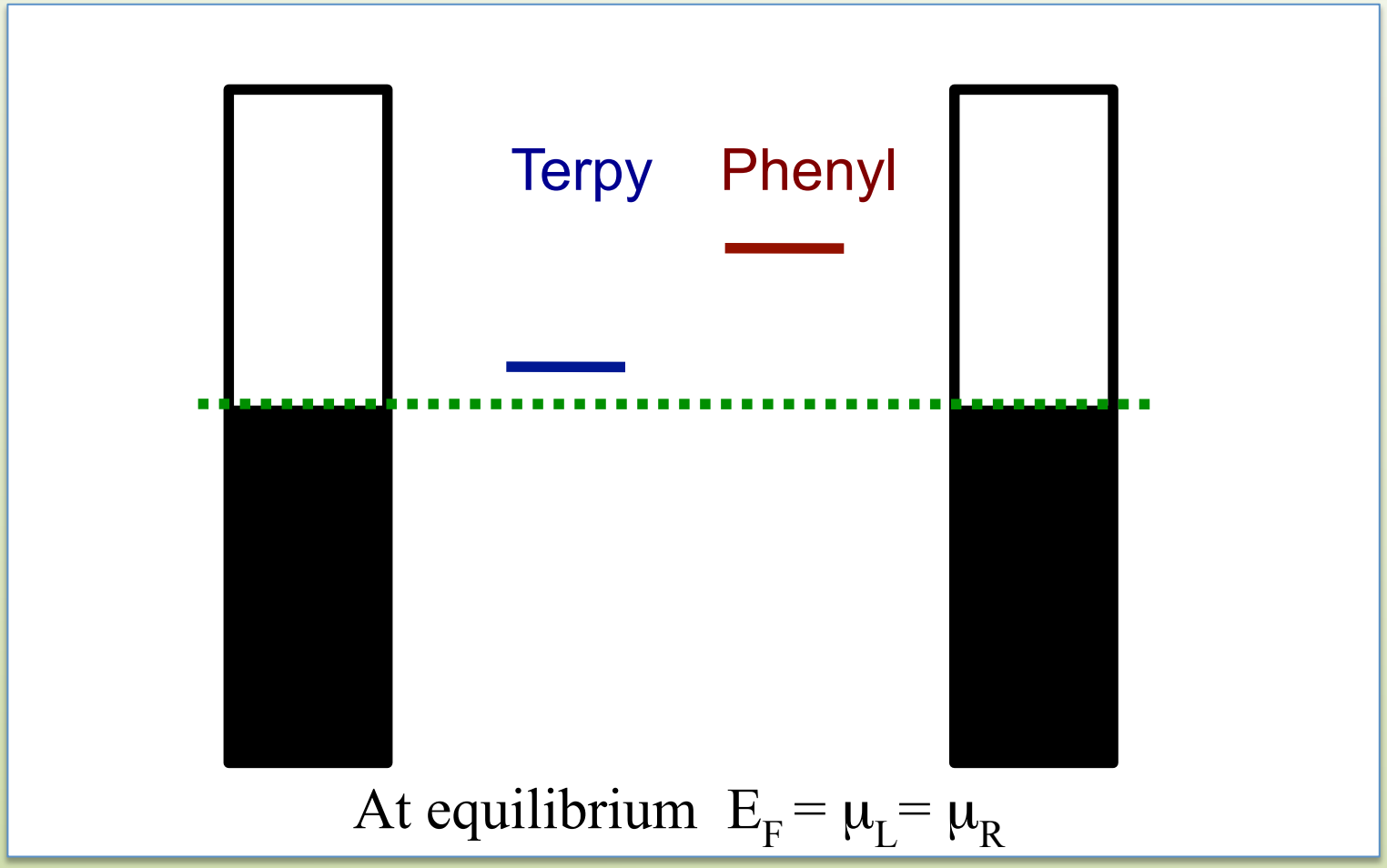


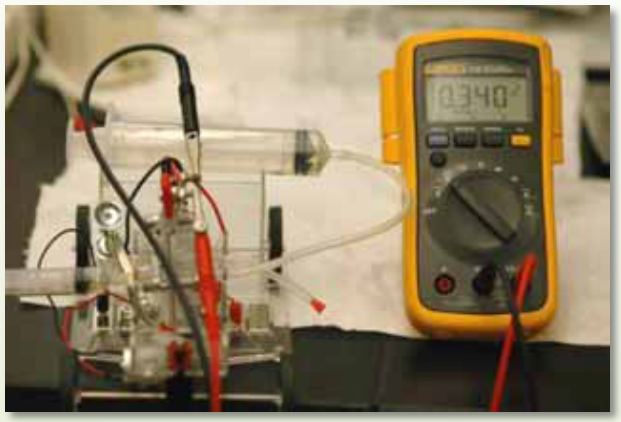




Molecular Rectification: DFT NEGF: I-V Characteristics

Aviram, M. A. Ratner Chem. *Phys. Lett.* **29**: 277-283 (1974)





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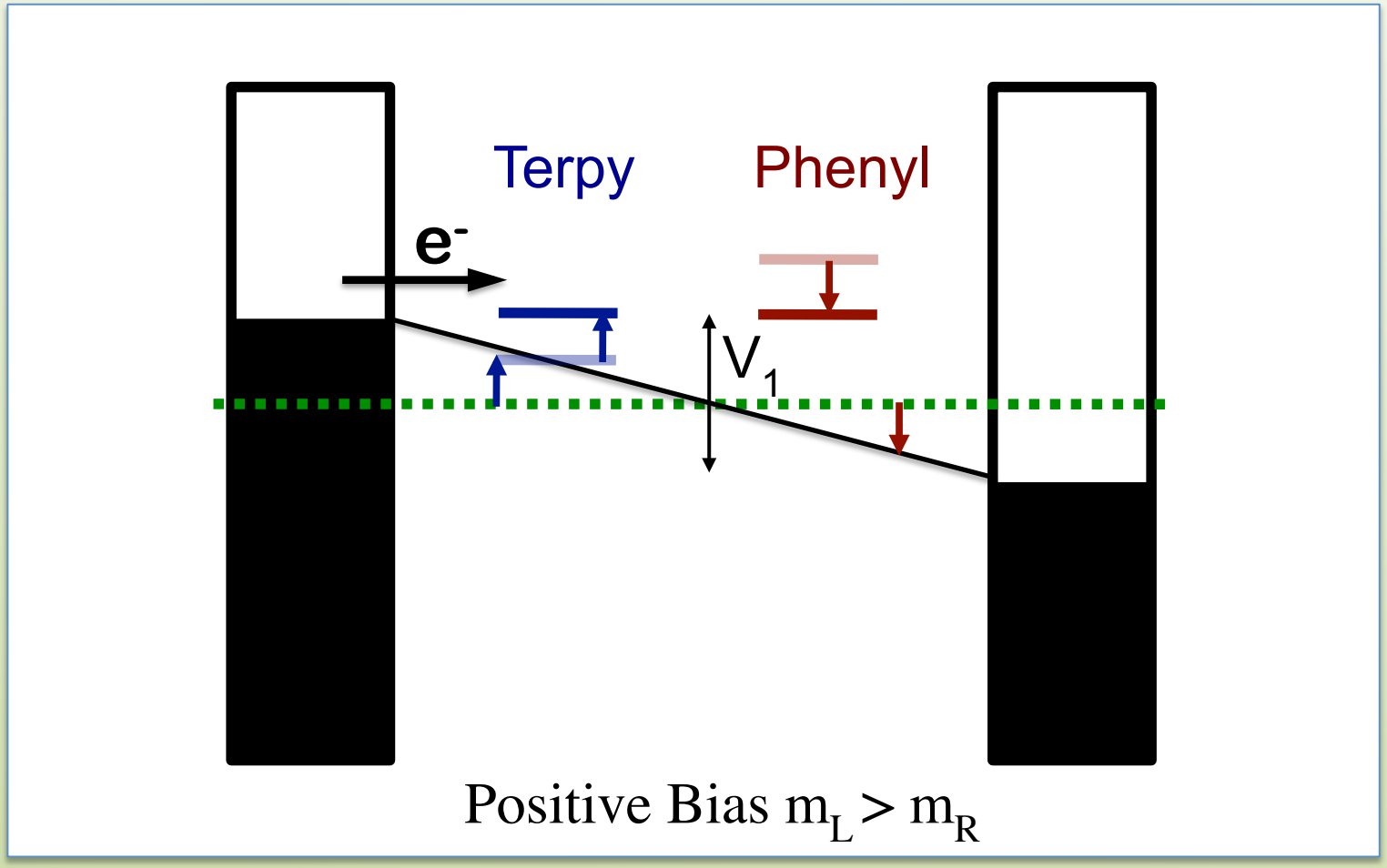

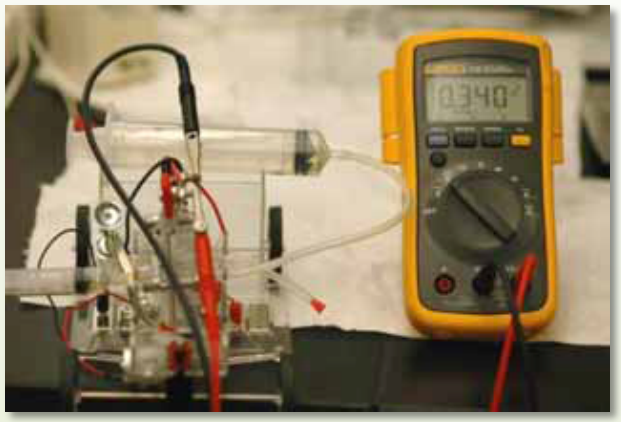

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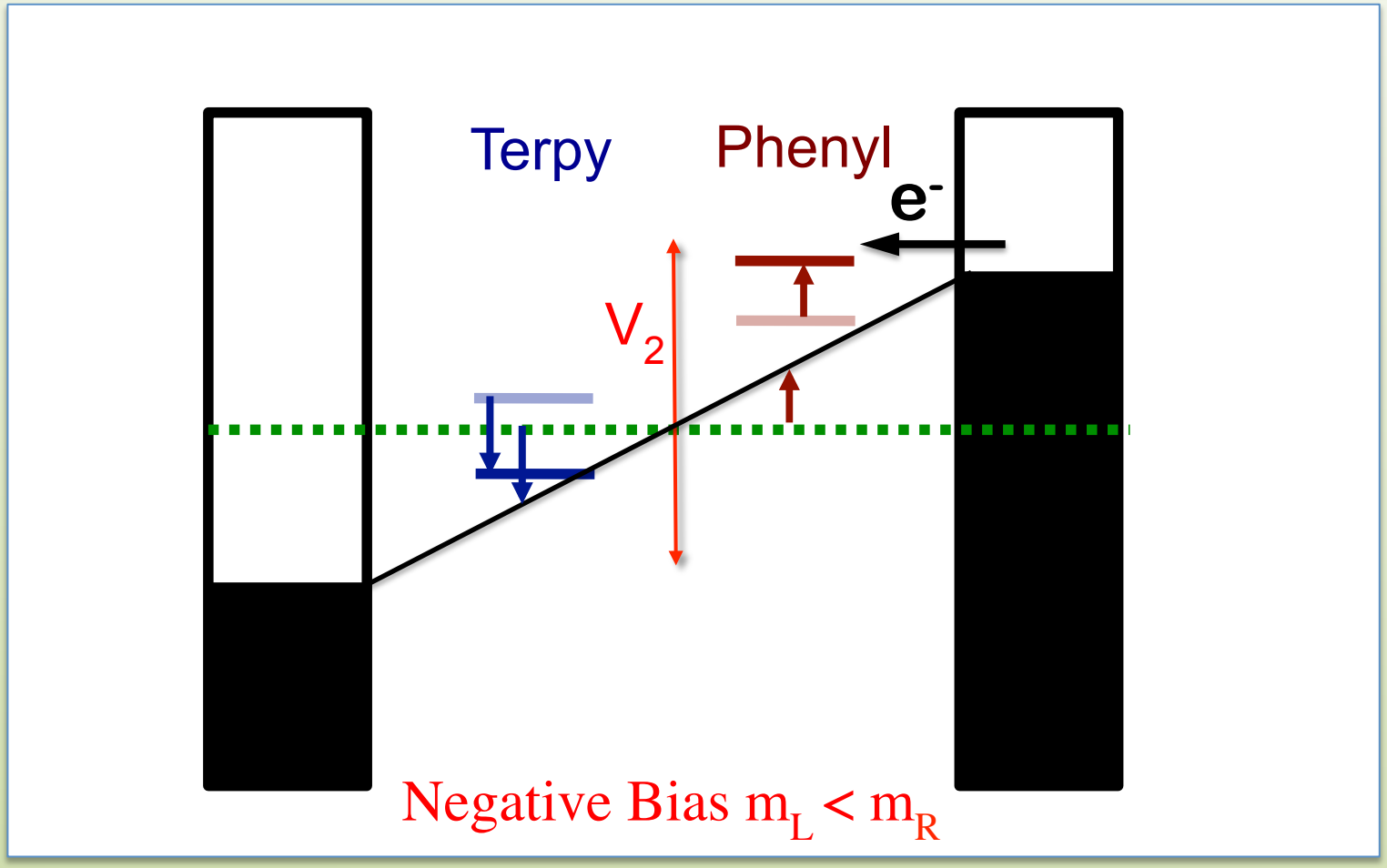
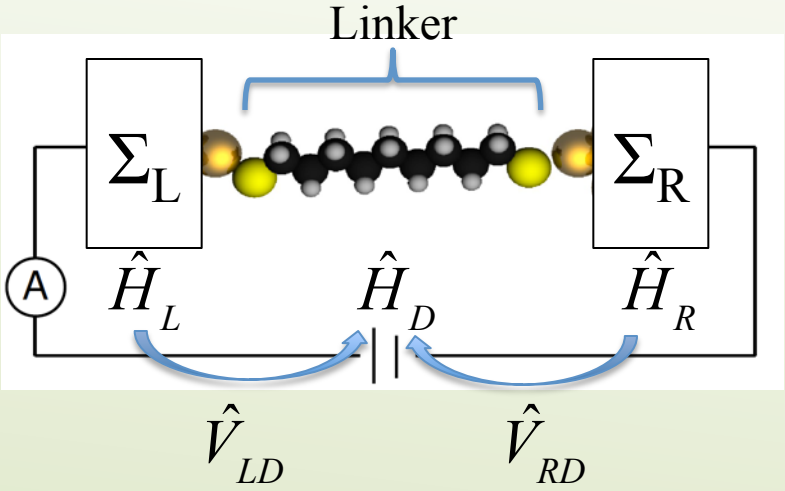


DFT-NEGF Methodology



$$\hat{H} = \begin{pmatrix} H_L & V_{LD} & 0 \\ V_{LD}^{+} & H_D & V_{RD}^{+} \\ 0 & V_{RD} & H_R \end{pmatrix}$$

$$\Sigma_{L/R} = \left(ES_{LD/RD}^{+} - V_{L/R}^{+}\right) g_{L/R} \left(ES_{LD/RD} - V_{L/R}\right)$$

$$\hat{H} \Rightarrow \hat{G} = \left(E\hat{S} - \hat{H} - \hat{\Sigma}\right)^{-1} \Rightarrow T(E) = Tr\left(\hat{\Gamma}_L \hat{G}_D \hat{\Gamma}_R \hat{G}_D^{+}\right) \Rightarrow \text{Current: } I$$

$$\hat{\Sigma} = \hat{\Sigma}_L + \hat{\Sigma}_R$$

$$G_D = \left(ES_D - H_D - \Sigma_L - \Sigma_R\right)^{-1}$$

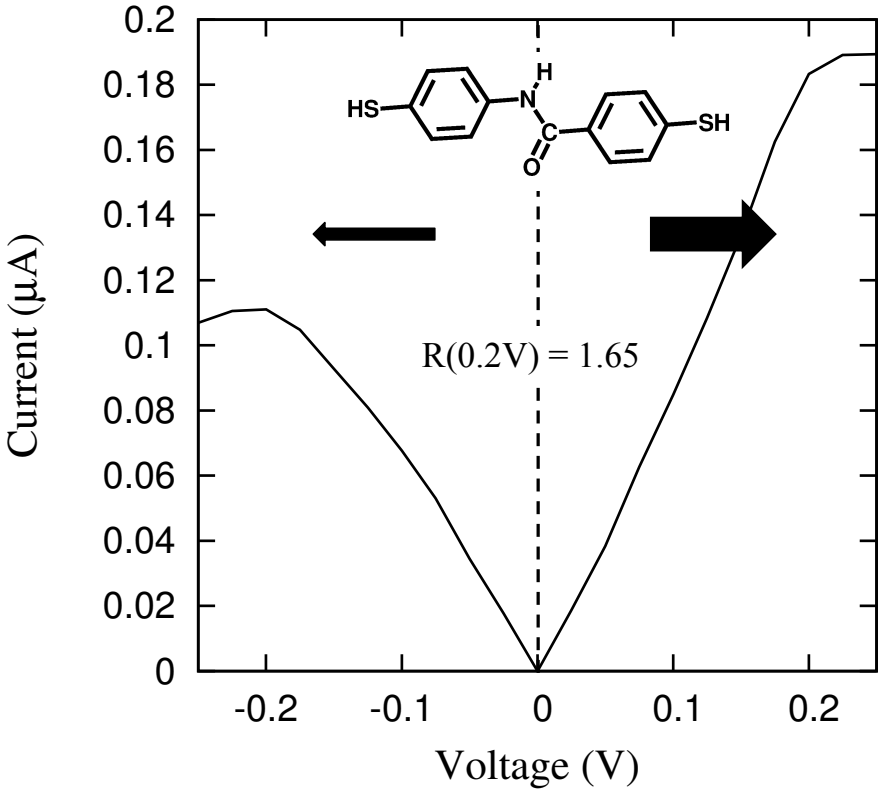
$$\Gamma_{L/R} = i\left(\Sigma_{L/R} - \Sigma_{L/R}^{+}\right)$$

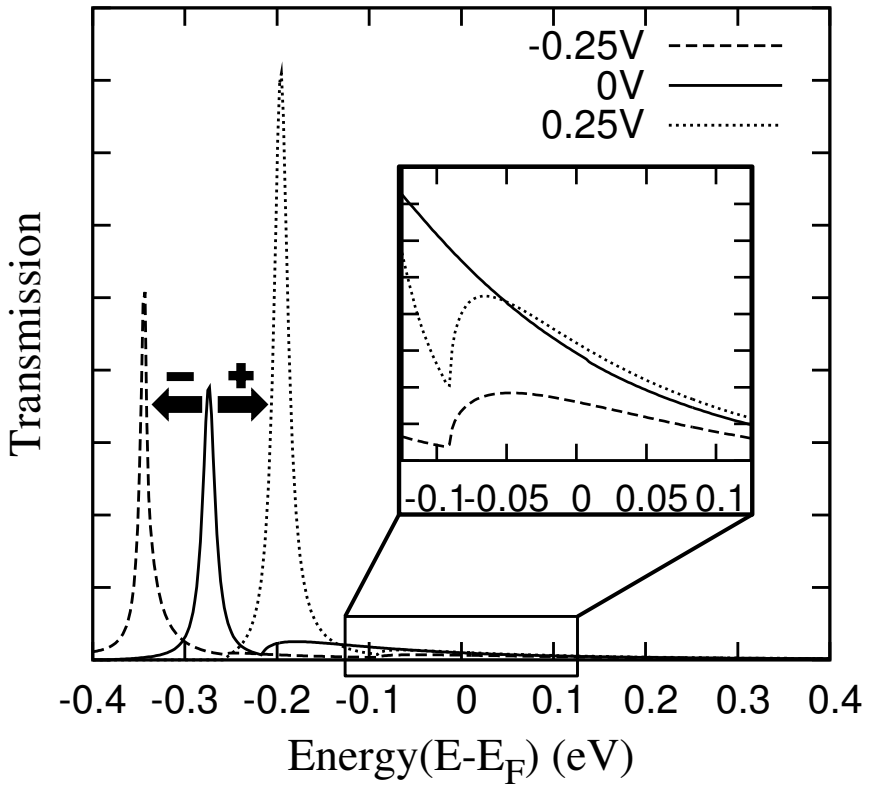
$$I = \frac{2e}{h}\int_{-\infty}^{\infty} dE\ T(E)\left[f_L(E) - f_R(E)\right]$$

$$\approx \frac{2e}{h}\int_{\mu_L}^{\mu_R} dE\ T(E)$$

MOLECULAR RECTIFICATION

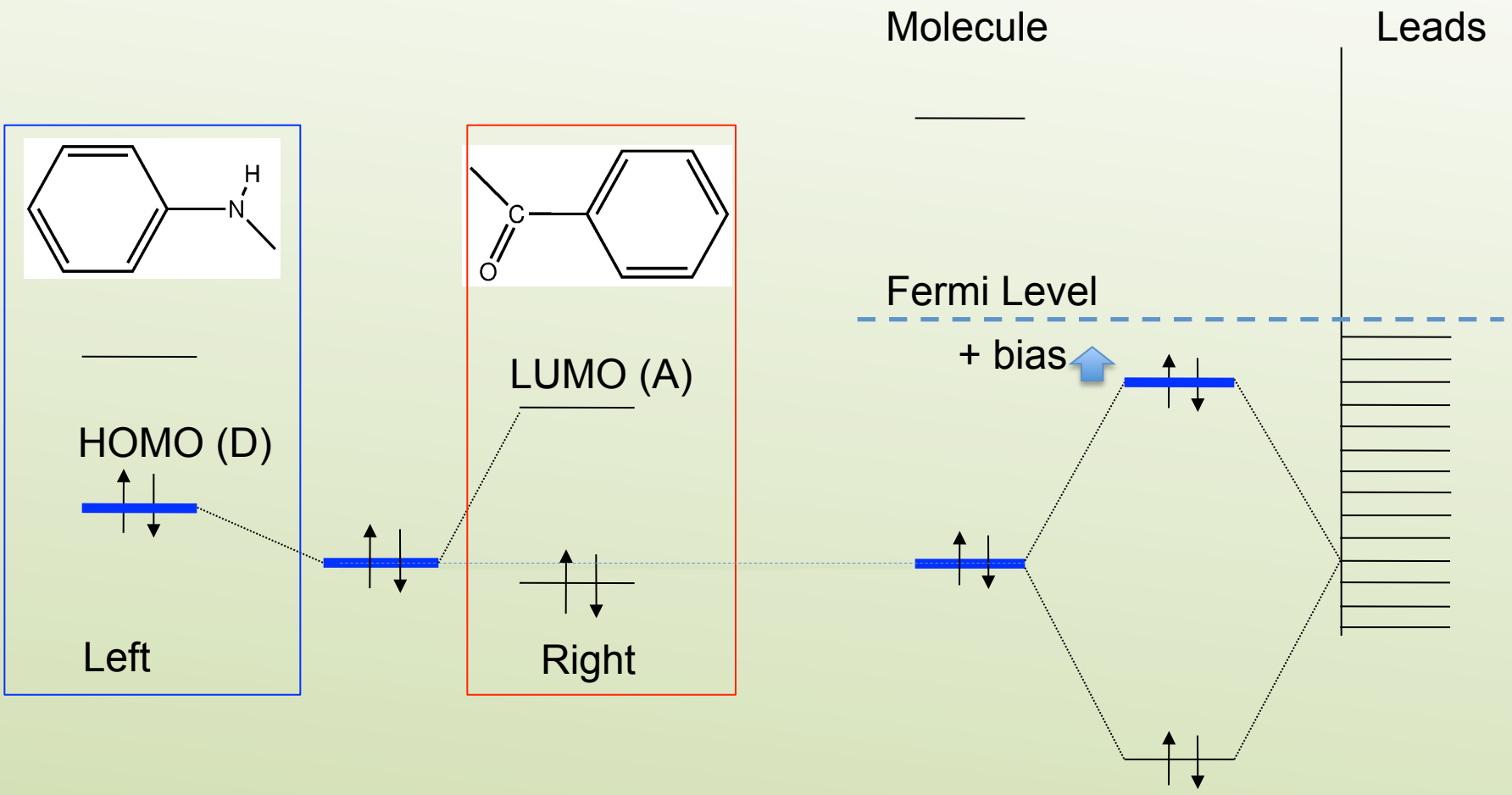
DFT NEGF: I-V Characteristics





Wendu Ding, Leslie Vogt, Christian F. A. Negre, and Victor S. Batista
[J. Chem. Theory Comput 10: 3393−3400 (2014)]

Molecule-Lead coupling



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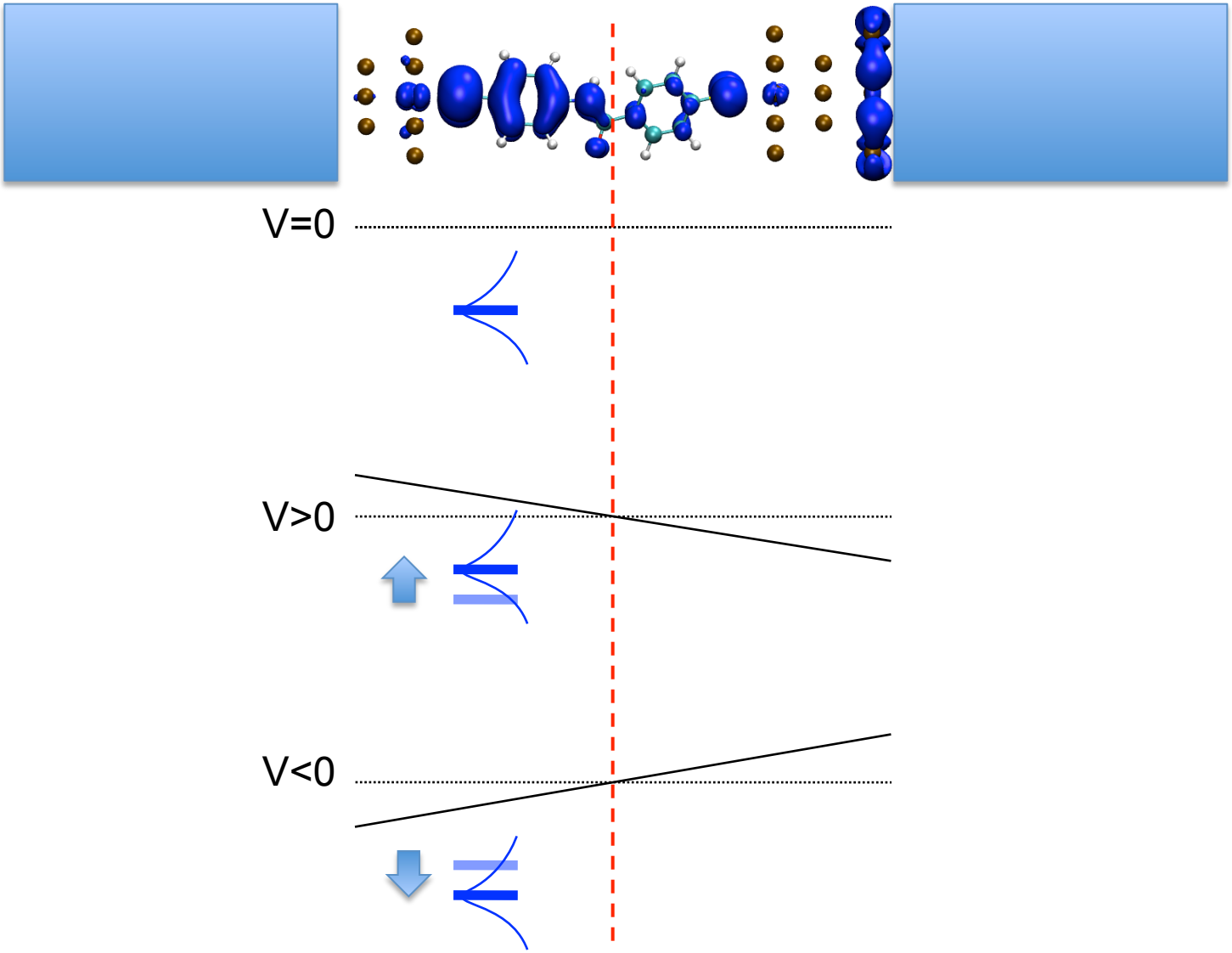
Single Frontier Orbital Mechanism



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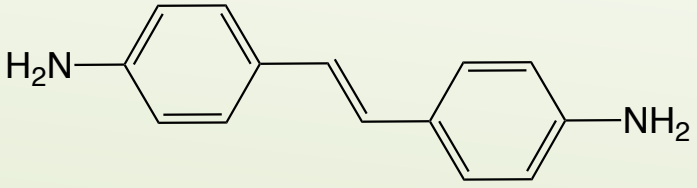
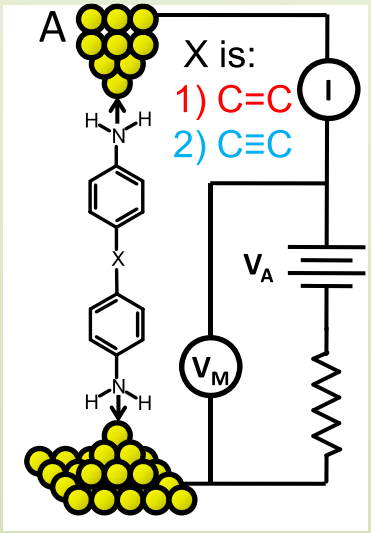
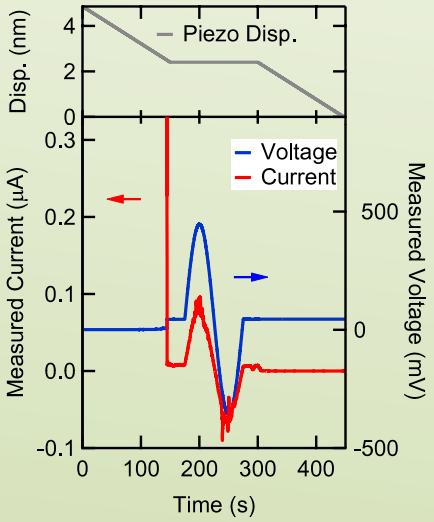
Experimental I-V histograms

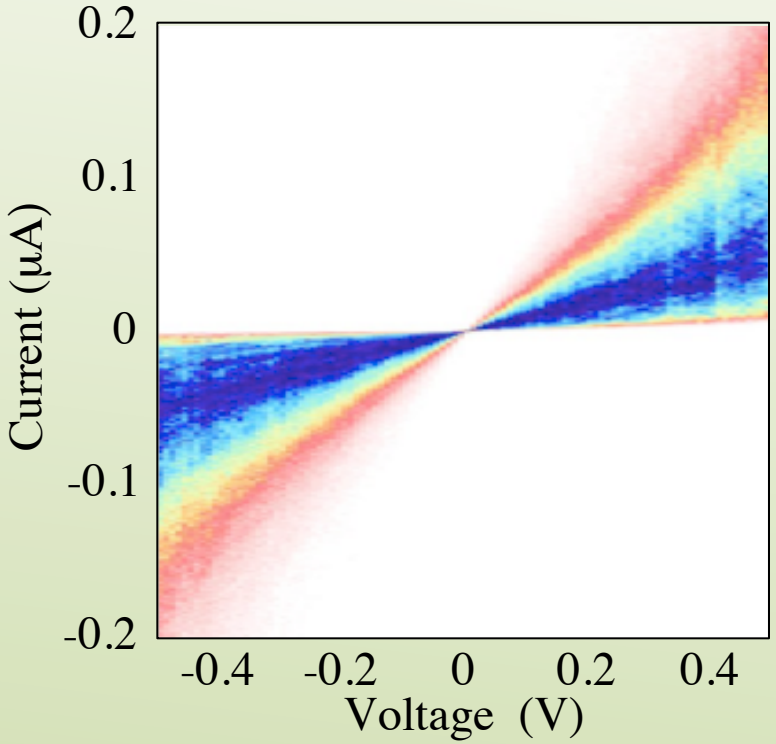
Prof. Latha Venkataraman
Columbia University

4,4'-Diaminostilbene



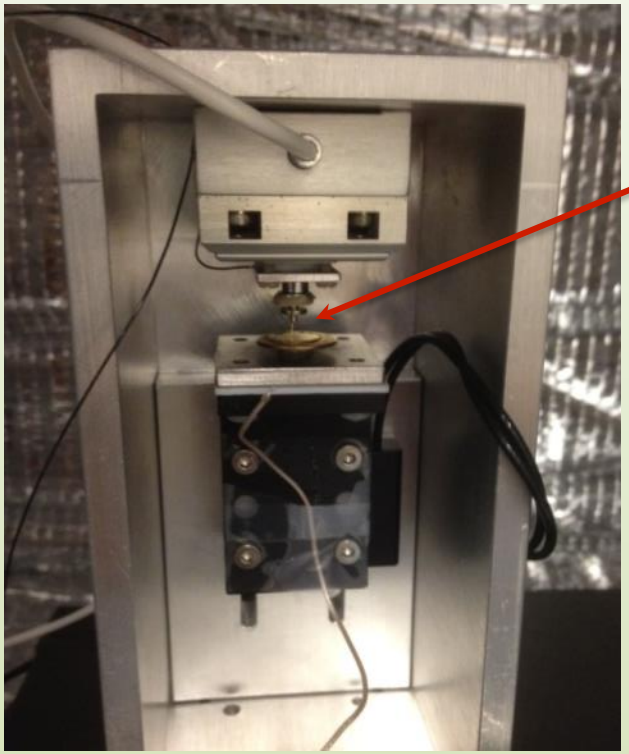


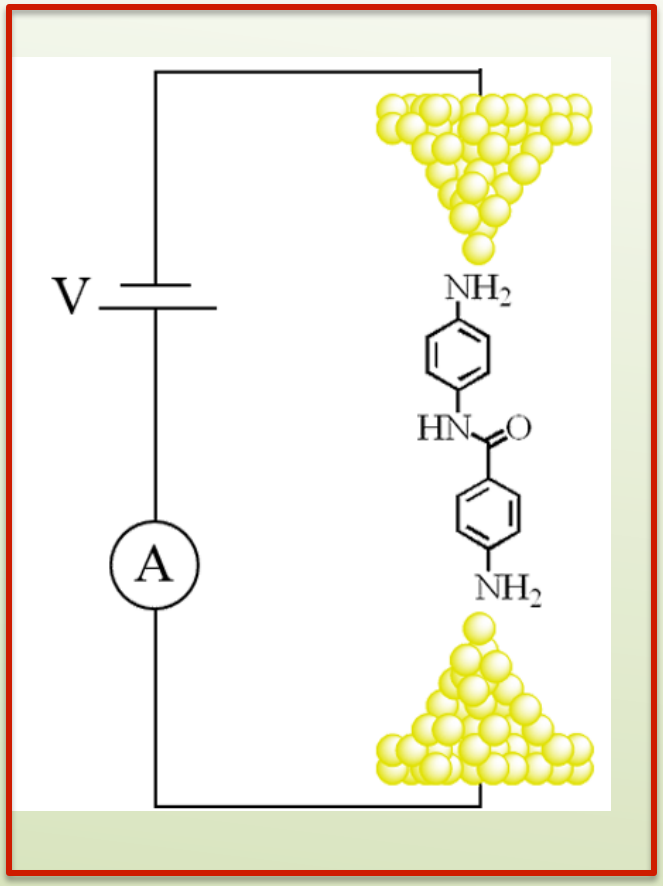




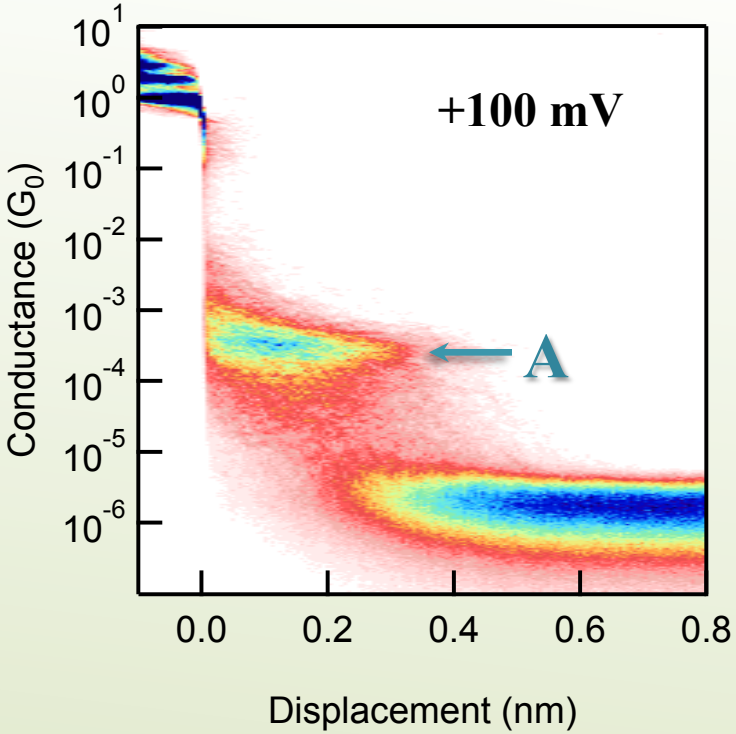
Nanotechnology. **2009**, *20*, 434009

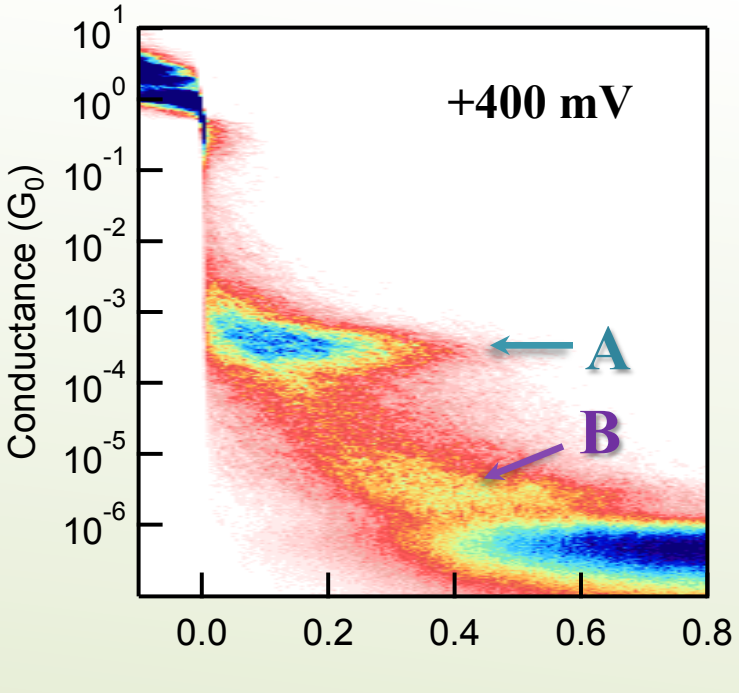
Molecular Rectification:
The Break Junction Technique & Recent Results



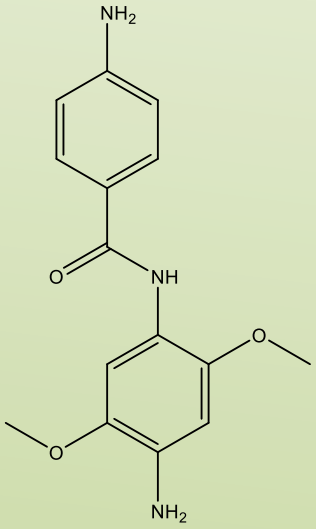


11-1-2013
Chris Koenigsmann

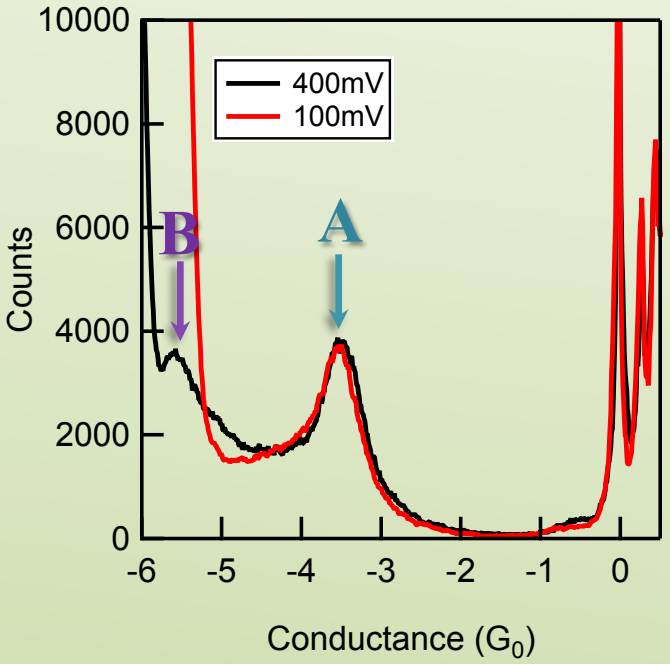




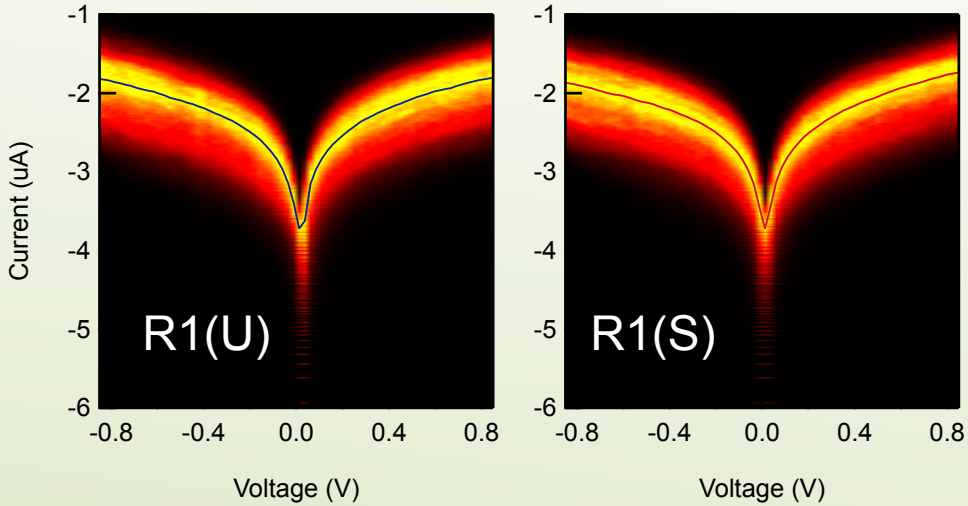
Molecule R5

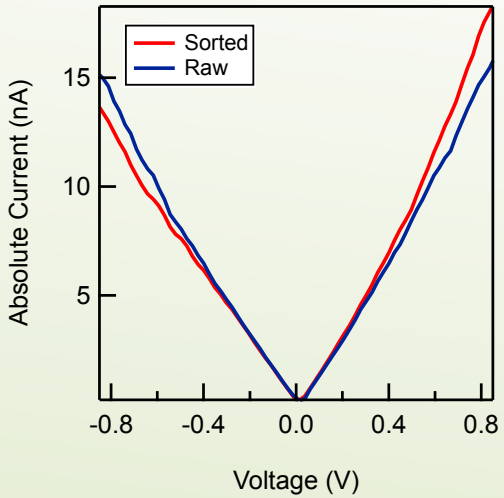


1. Well defined single molecule conductance plateaus (A).
2. Conductance ~2.9 x 10^{-4} G_0
3. Small but measureable increase in conductance as bias increases.
4. A second low-conductance plateau (B) also observed (+400 mV).

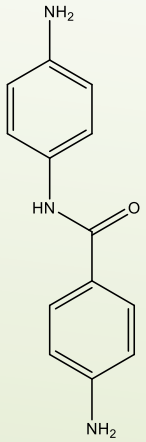


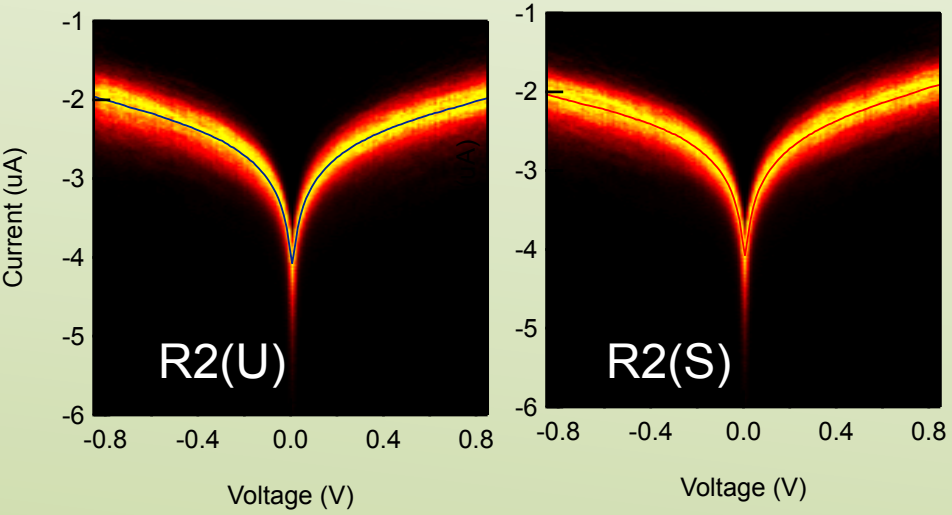
Experimental and Theoretical IV curves

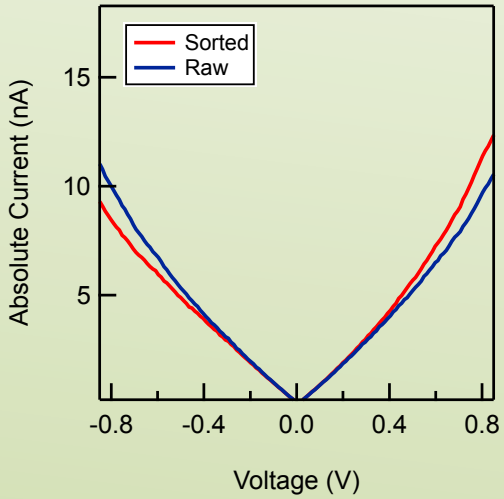




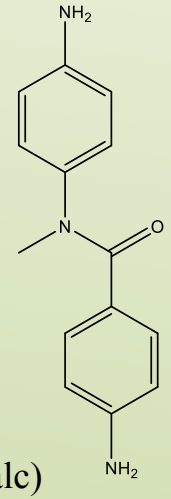
RR@0.85V =1.3







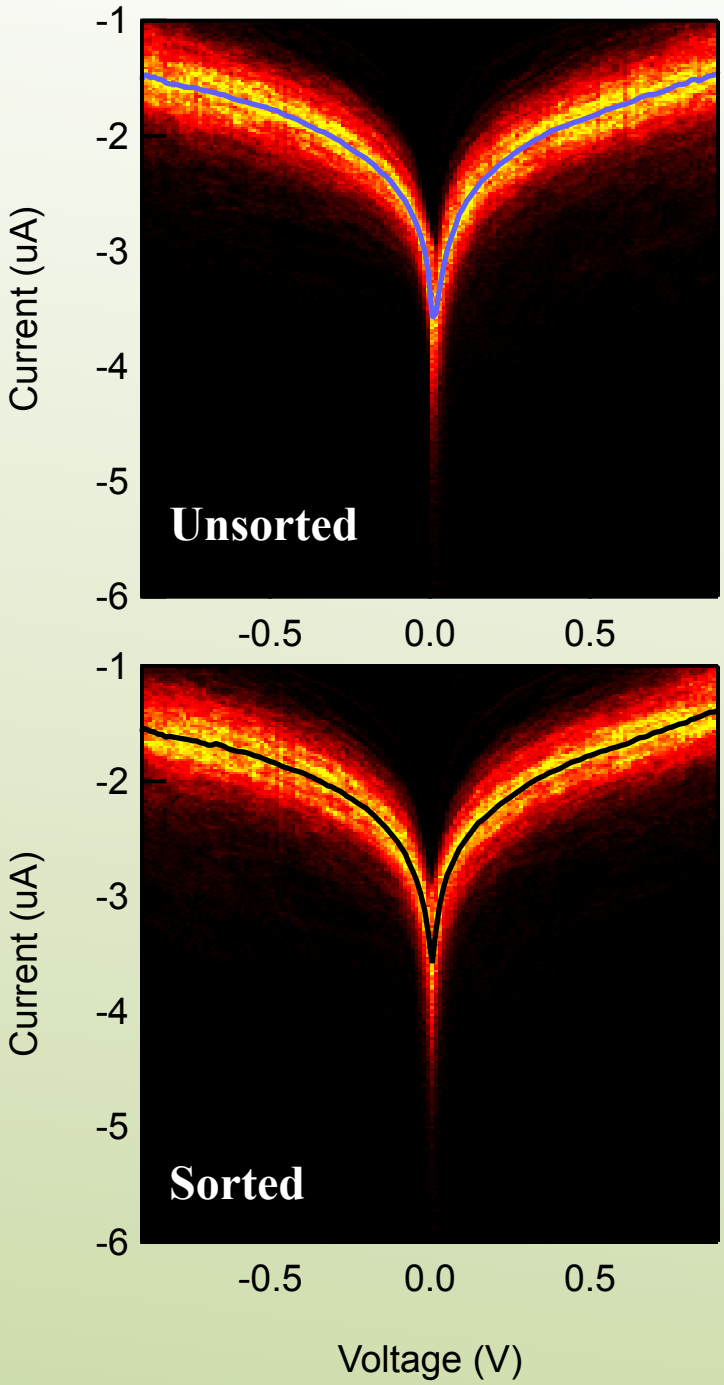
RR@0.85V =1.33

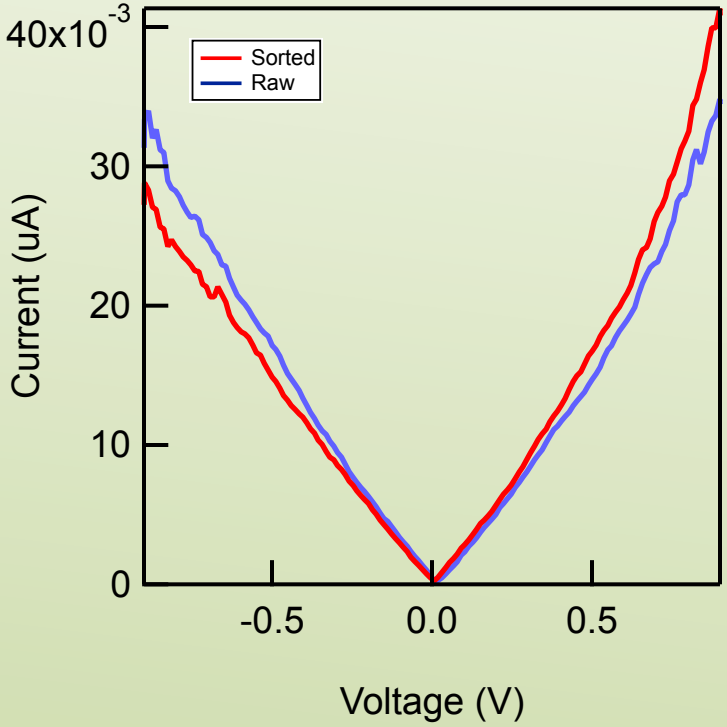


Latha Venkataraman, Chris Koeningsmann (I-V exp), Matthieu Koepf (synthesis), Christian Negre (I-V calc)

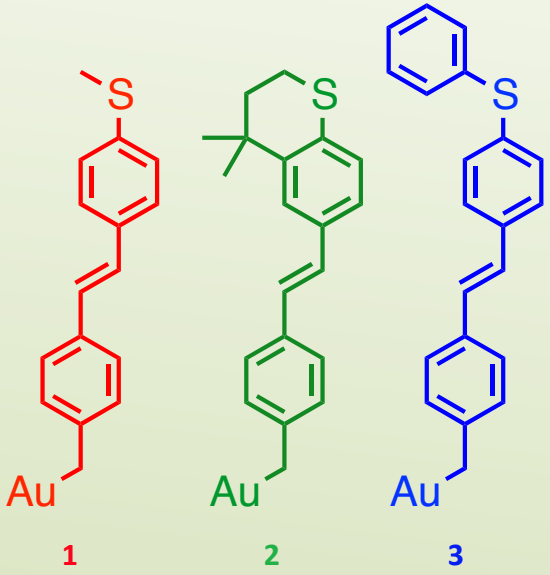
R5, Rectification at 0.85 V = 1.45

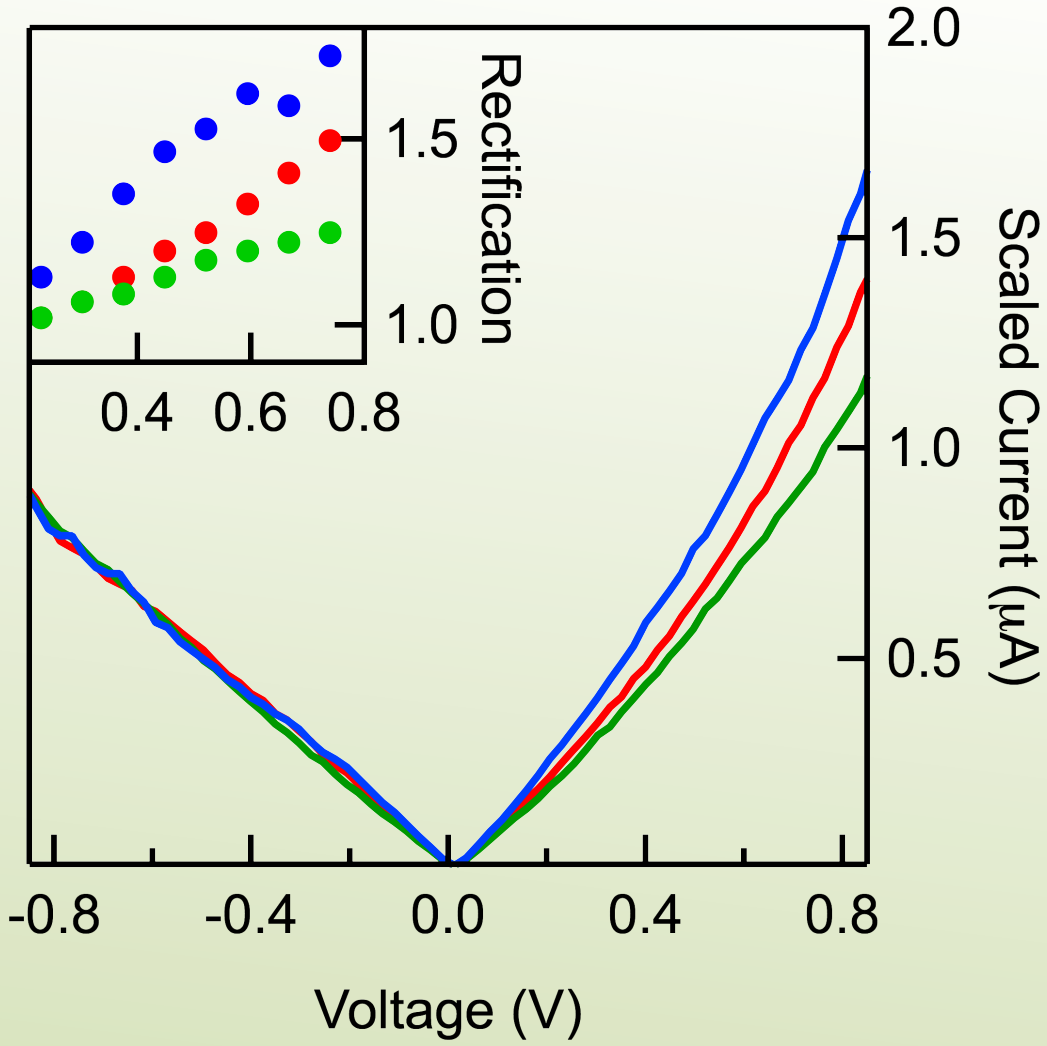
Molecule	Conductance (G_0)	RR
R1	1.7×10^{-4}	1.30
R5	2.9×10^{-4}	1.45



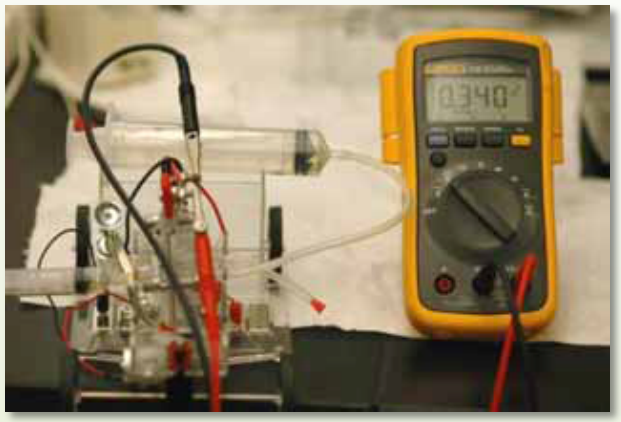


Examples of Rectifying & Poor-Rectifying Molecules





Scaled, statistically most probable IV curves for the three molecules. The curves are calculated from log-binned 2D histograms with bin sizes and histogram ranges kept constant. All curves have been scaled to zero-bias conductance of molecule **3**, with the red curve multiplied by 2 and the blue curve by 4. Inset: Rectification ratio as a function of bias. Molecule **3** rectifies over three times as much as molecule **2**, with rectification at 0.85V approaching 2.



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Molecular Inverse Design: LCAP Methodology

Dr. Dequan Xiao

Schrödinger equation in EH matrix form is

$$\mathbf{HC} = \mathbf{ESC}$$

Hamiltonian matrix; Eigenvector matrix; Eigenvalue matrix (diagonal matrix); Overlap matrix (AO basis set)

LCAP-EHTB:

Diagonal terms

$$H_{ii}^{(\mathrm{var})} = \sum_{A=1}^{N_{type}^{i}} b_A^i h_{ii}^{(A)}$$

Off-diagonal terms

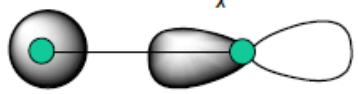
$$H_{ij} = \sum_{A=1}^{N_{type}^{i}} \sum_{A'=1}^{N_{type}^{j}} b_A^i b_{A'}^j h_{ij}^{(A,A')}$$

constraints

$$0 \le b_A^i \le 1$$

$$\sum_{A=1}^{N_{type}^{i}} b_A^i = 1$$

Example:



1 2

O C, O

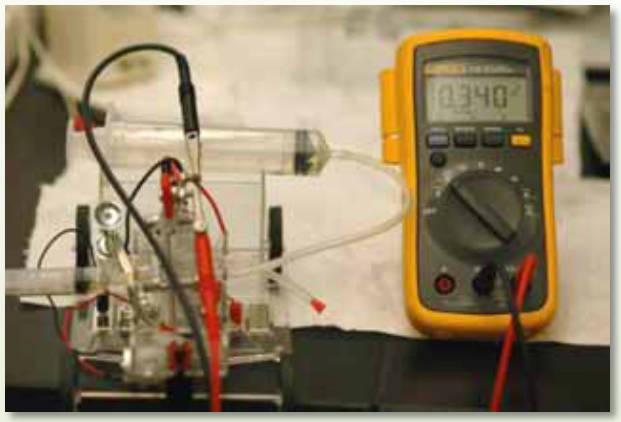
b_C^2 b_O^2

Diagonal term

$$H_{22}^{P_x} = b_C^2 \cdot h_{22}^{(C_{P_x})} + b_O^2 \cdot h_{22}^{(O_{P_x})}$$

Off-diagonal term

$$H_{12}^{SP_x} = b_O^1 \cdot b_C^2 \cdot h_{12}^{(O_S, C_{P_x})} + b_O^1 \cdot b_O^2 \cdot h_{22}^{(O_S, O_{P_x})}$$



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Modeling Systems for a Hydrogen Economy

Inverse Design: Molecular Sensitizers

Target molecular property: the total visible absorbance

Dr. Dequan Xiao

$$f = \sum_{p,q} f_{pq} \quad \text{+ constraint: } 400nm \le \lambda_{qp} \le 800nm$$

f_{pq} is the oscillator strength of the p to q electronic transition, and λ_{pq} is the wavelength of the electronic transition.

$$f_{pq} = \frac{8\pi^2 \nu_{pq} m_e}{3he^2} \left|\mu_{pq}\right|^2$$

$\mu_{pq} = \langle \psi_q | r | \psi_p \rangle$: transition dipole moment,

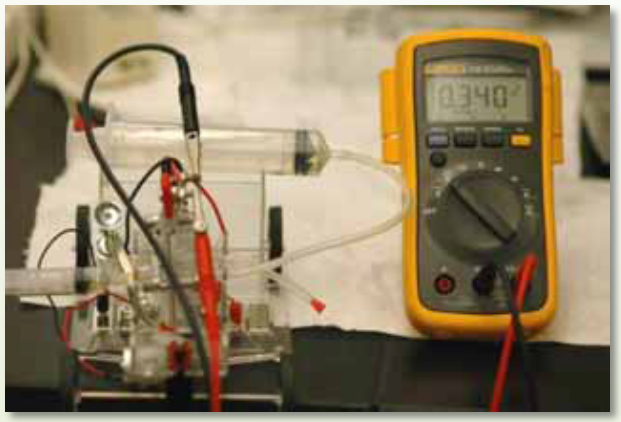
ν_{pq} : wavenumber of the electronic transition,

m_e : electron mass.

Gradients of molecular property:

$$\frac{\partial f}{\partial b_A^i} = \frac{f(+\delta b_A^i) - f(-\delta b_A^i)}{2\delta b_A^i}$$

Finally, the **continuous optimization** of *f* by varying $\{b_A^i\}$ is performed based on a quasi-Newton (BFGS algorithm) method.



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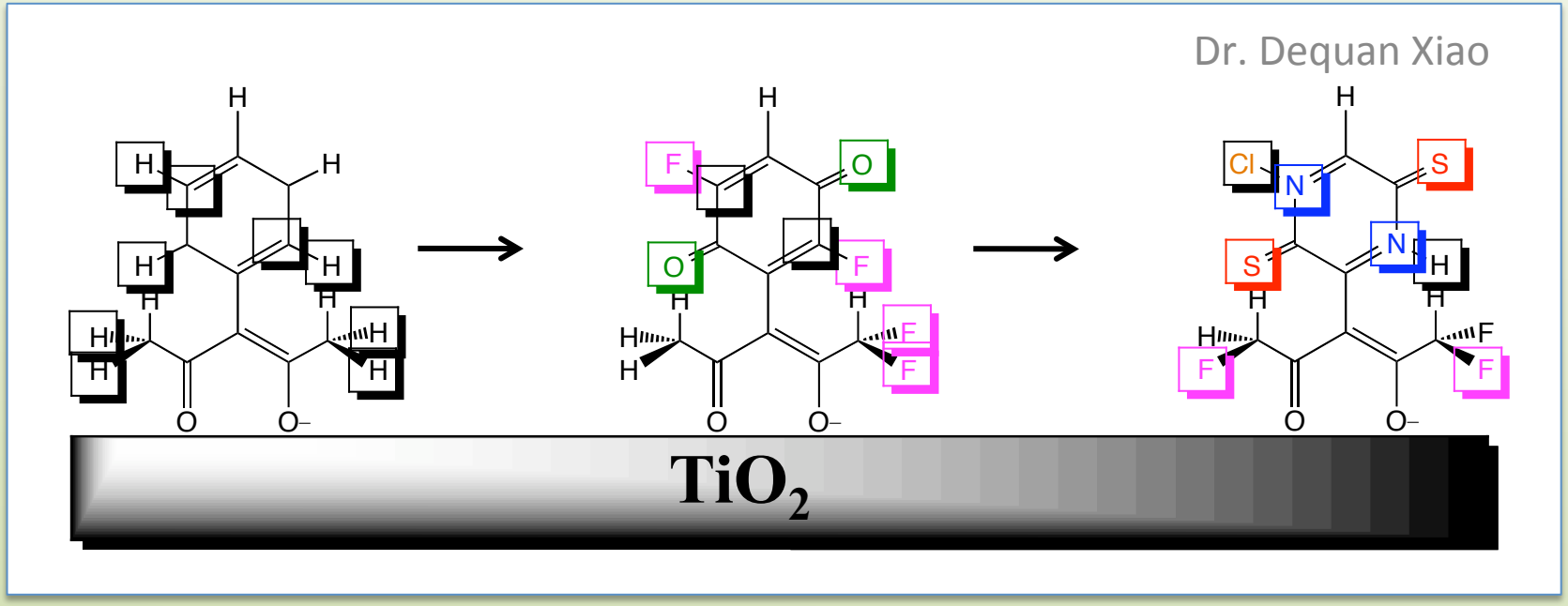
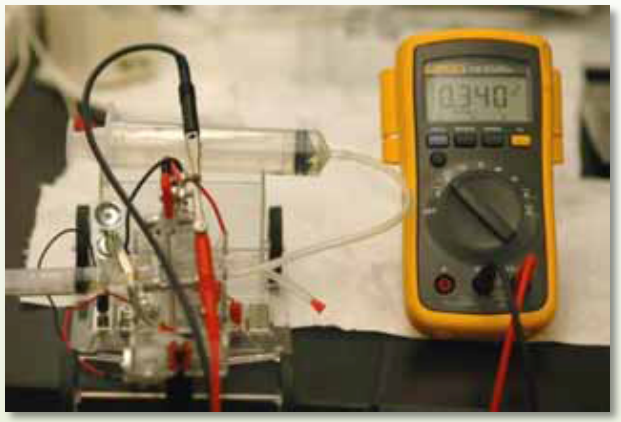
Inverse Design: Molecular Sensitizers





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Inverse Design: Molecular Sensitizers

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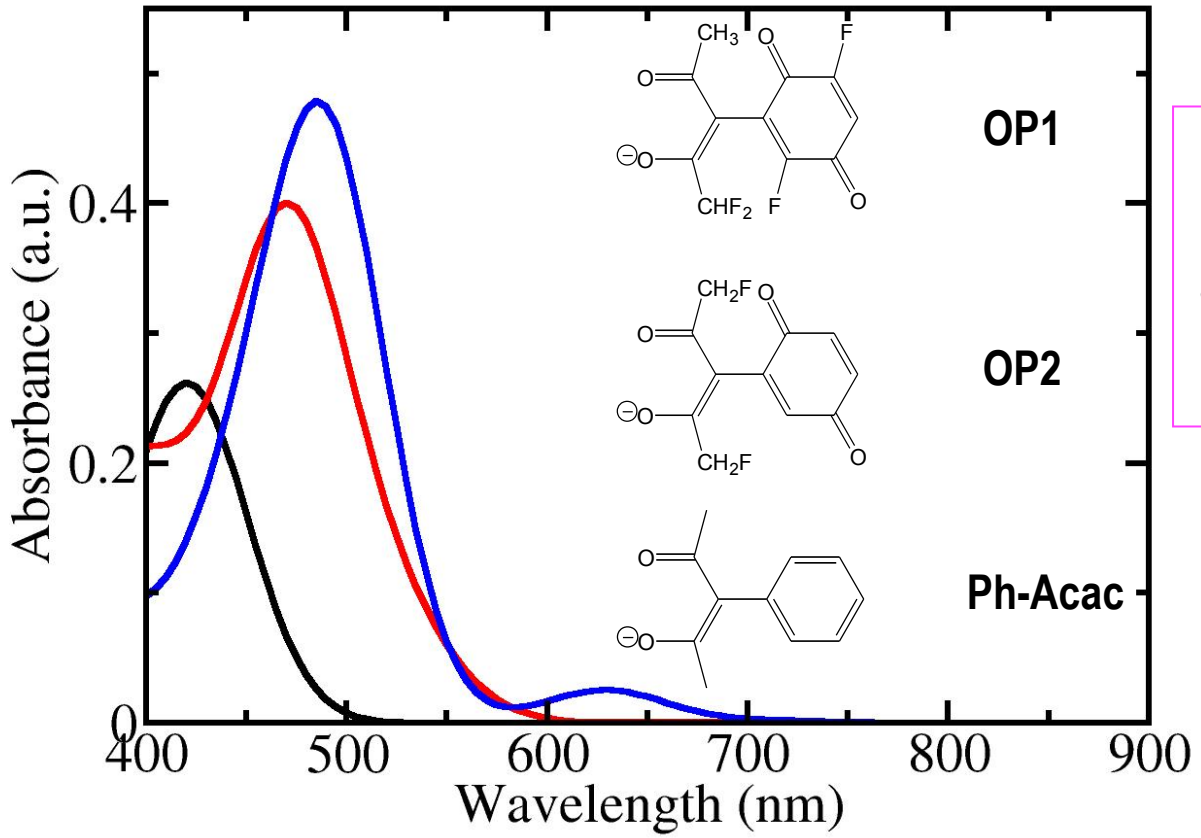
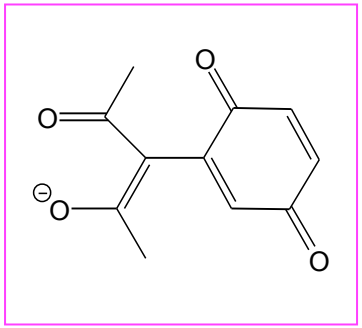
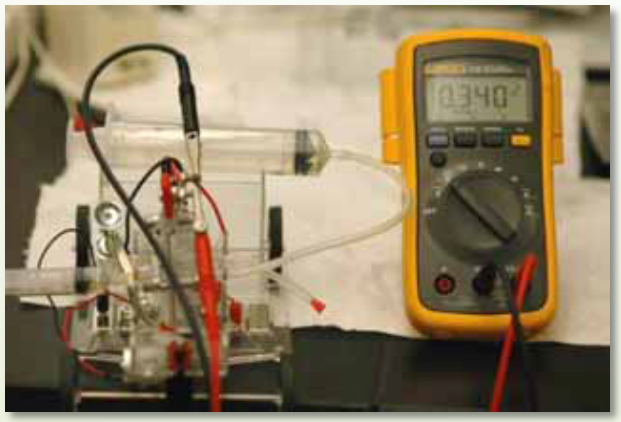




OP

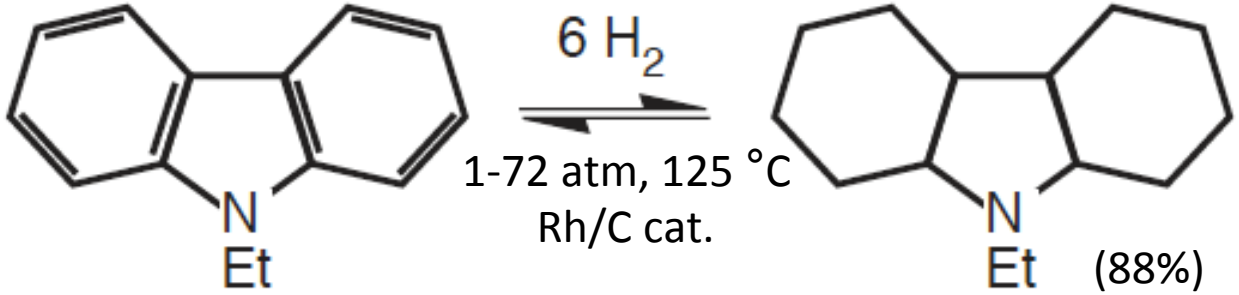


CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

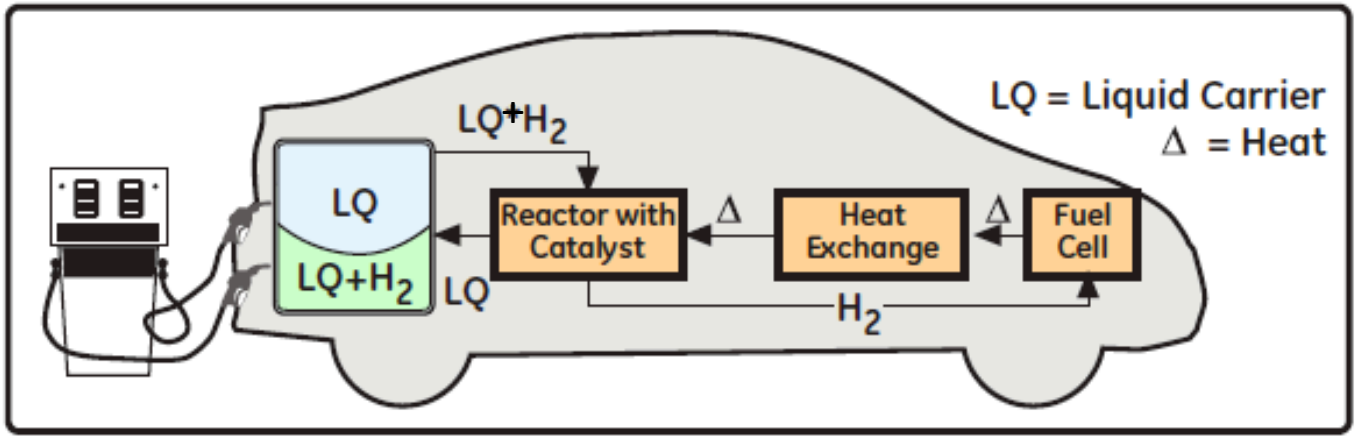
Modeling Systems for a Hydrogen Economy

Liquid H-Carriers: Fuel Cell/Flow Battery Concept

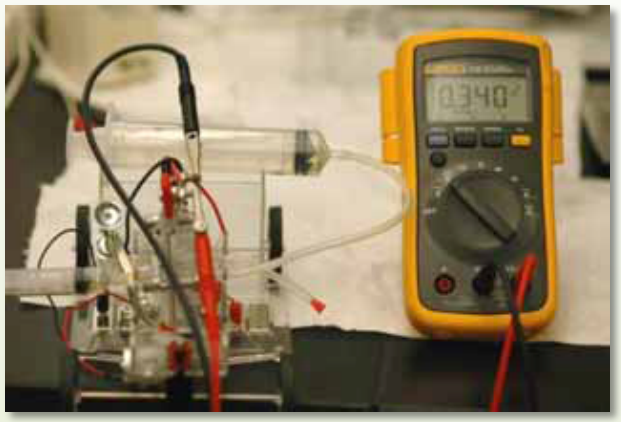
Thermal (de)hydrogenation



G. P. Pez, A. R. Scott, A. C. Cooper and H. Cheng, *US patent*, 7101530 (2006)



Courtesy AIR PRODUCTS



CHEM 505: *Green Chemistry and Alternative Energy*

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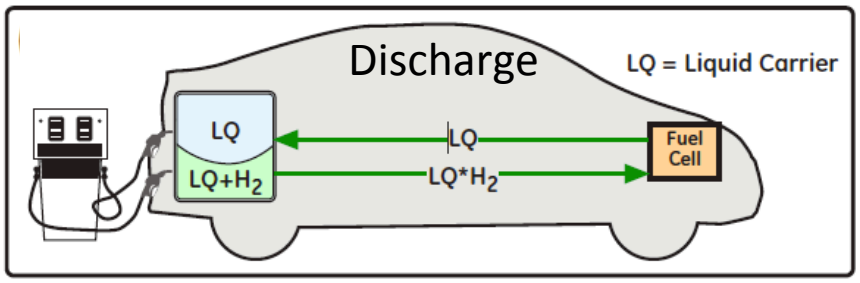
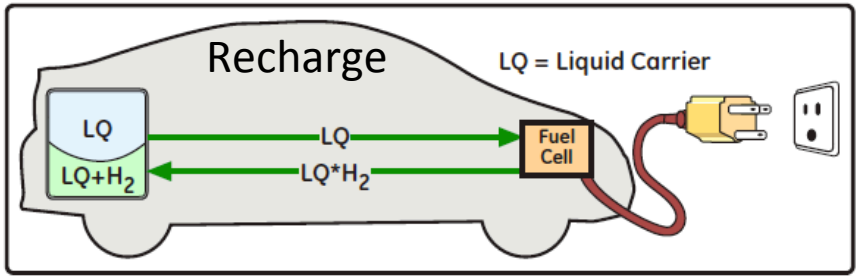
Modeling Systems for a Hydrogen Economy

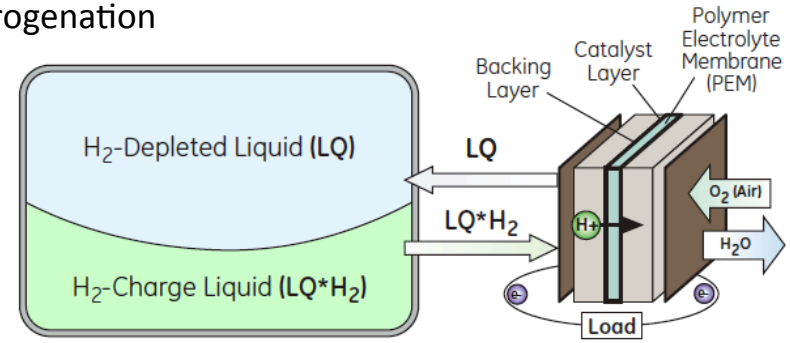
Organic Fuel Cell/Flow Battery Concept

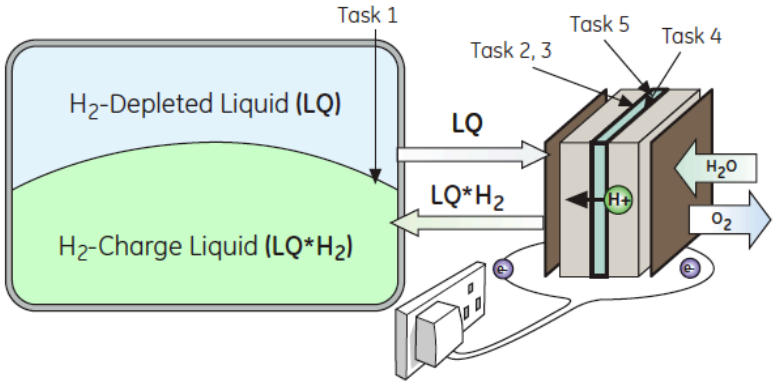
"Feed the hydrogenated organic liquid carrier directly into the fuel cell where it is electrochemically dehydrogenated without ever generating H_2"

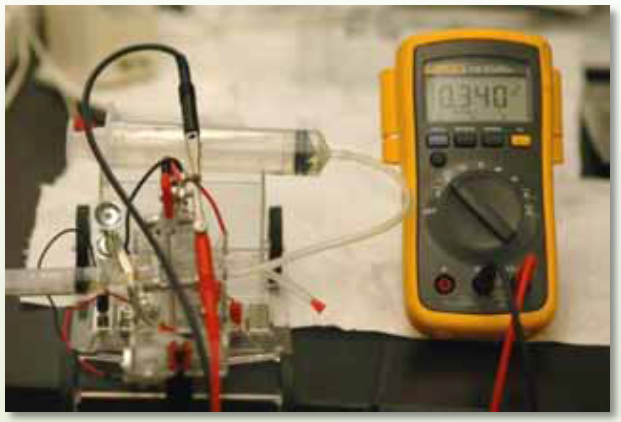
Electrochemical (de)hydrogenation











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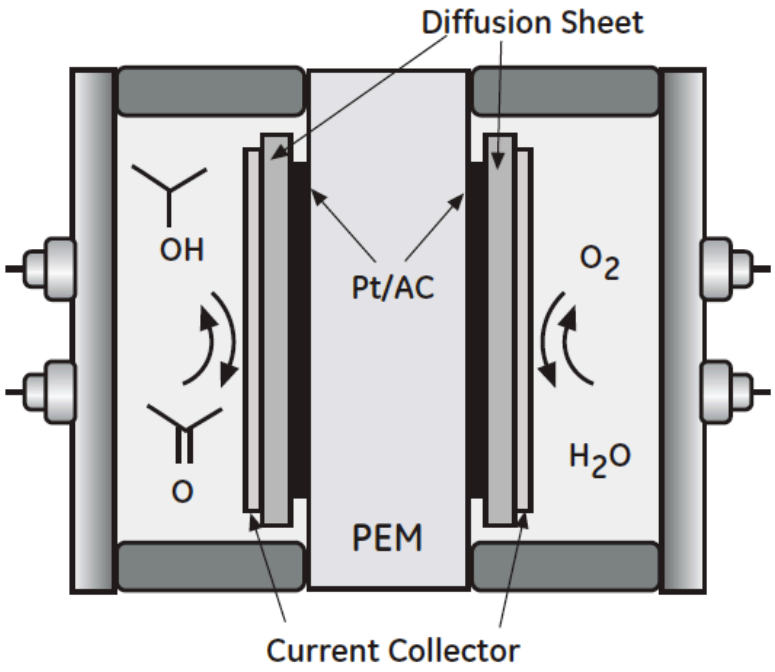
Modeling Systems for a Hydrogen Economy

Organic Fuel Cell/Flow Battery Concept

"Electrochemical dehydrogenation can be done at lower temperatures and high rates"



$$LQ^*H_n \rightarrow LQ + n\,H^+ + n\,e^- \quad (1)$$

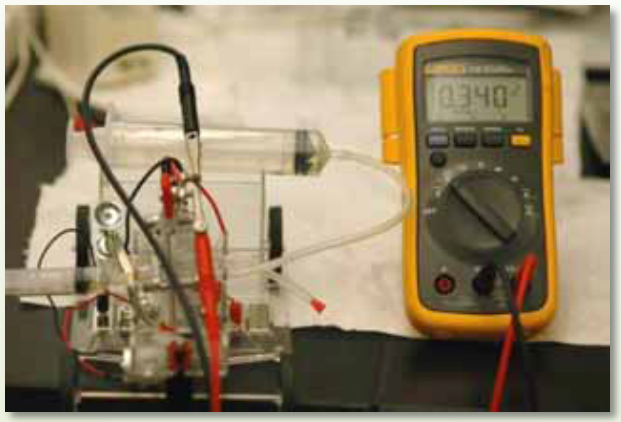
$$n/2\,O_2 + n\,H^+ \rightarrow n/2\,H_2O - n\,e^- \quad (2)$$

$$LQ^*H_n + n/2\,O_2 \rightarrow n/2\,H_2O + LQ \quad (3)$$

*where LQ stands for an organic carrier molecule

Electrochemical dehydrogenation of saturated cyclic hydrocarbons (e.g., cyclohexane and decaline) is possible in alkaline electrolyte using Pd and Rh catalysts.

[K.V. Kordesch, J.F. Yeager, J.S. Dereska, *US Patent* 3280014 (1966); M. Okimoto, Y. Takahashi, K. Numata, G. Sasaki, *Heterocycles*, **65** (2005) 371]



CHEM 505: *Green Chemistry and Alternative Energy*

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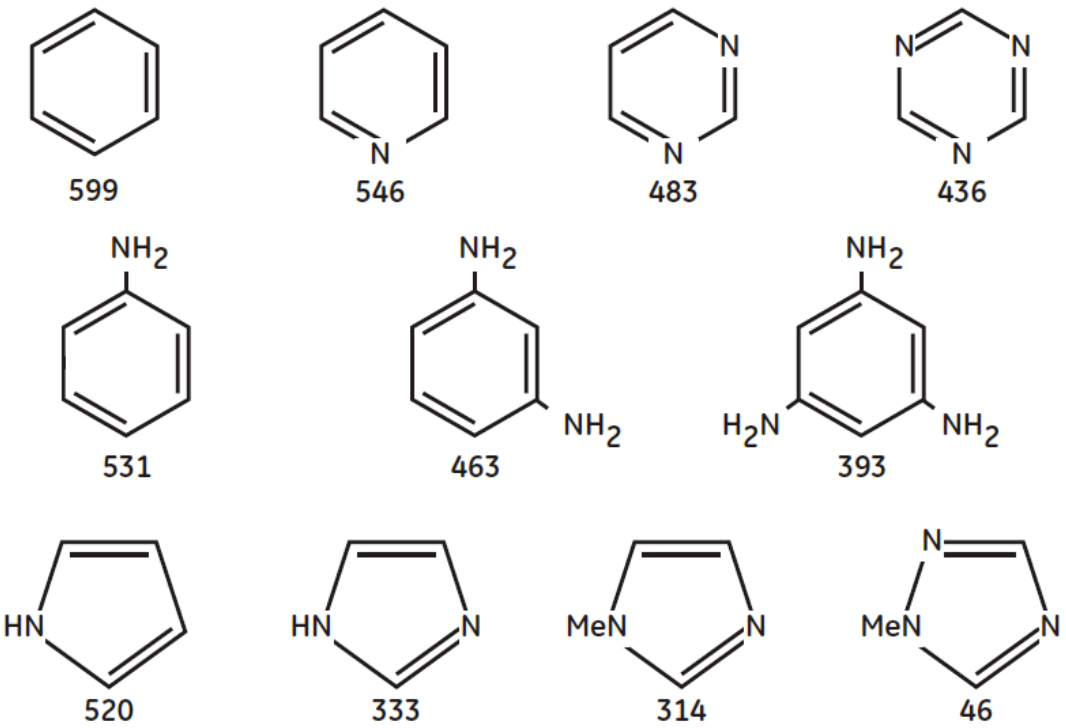
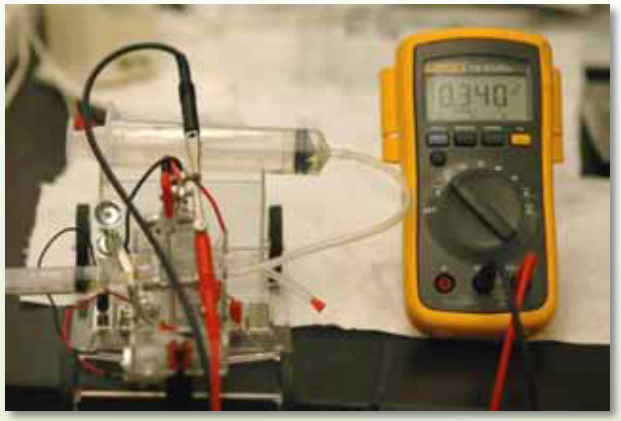
Modeling Systems for a Hydrogen Economy

Organic Liquid H-Carriers

Temperature (K) for spontaneous (de)hydrogenation ΔG = 0 (DFT B3PW91)



E. Clot, O. Eisenstein, R.H. Crabtree, *Chem. Commun*. 22:2231-2233 (2007).



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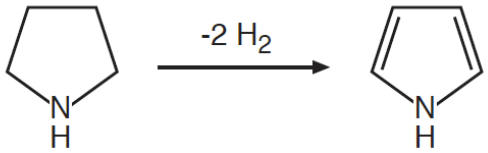
Modeling Systems for a Hydrogen Economy

Organic Liquid H-Carriers

Exercise 4:

Nitrogen atoms introduced into heterocycles tune the thermodynamic tendency to absorb or release H_2, or to absorb or release 2(H+ and e-). A particularly favorable condition is when aromatic stabilization can be achieved after cleavage of only four C-H bonds as in the following reaction:



This can be analyzed by computing the temperature $T = T_d$ that makes the dehydrogenation free energy $\Delta G = \Delta H - T\,\Delta S$ equal to zero. At this point ($T = T_d$) the unfavorable enthalpy due to the endothermicity of the reaction is exactly compensated by the favorable entropy of H_2 release.

(a) Find the minimum energy configurations of reactants and products for the dehydrogenation reaction shown above in the gas-phase at the DFT B3PW91 level of theory.

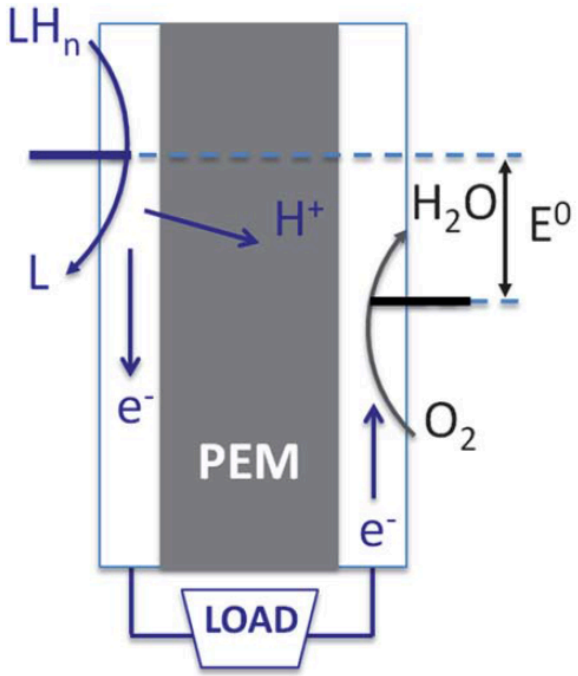
(b) Perform a frequency calculation for reactants and products and compute the temperature T_d at which the dehydrogenation becomes spontaneous.

(c) Compare your results with the analogous calculation of dehydrogenation T_d for cyclopentane.

Solution Exercise 4: See tutorial notes on ab initio free energy calculations.

Organic fuel cell/flow battery: Fuel selection from thermodynamic considerations Energy Env Sci 5: 9534-9542 (2012)

C. Moyses Araujo, Davide L. Simone, Steven J. Konezny, Aaron Shim ,
Robert H. Crabtree, Grigorii L. Soloveichik, and Victor S. Batista



$$LH_n \leftrightarrow L + nH^+ + ne^-$$

$$+\ n/4\ O_2 + nH^+ \leftrightarrow n/2\ H_2O - ne^-$$

$$LH_n + n/4\ O_2 \leftrightarrow L + n/2\ H_2O$$

$$E^0 = -\Delta G_r/nF$$

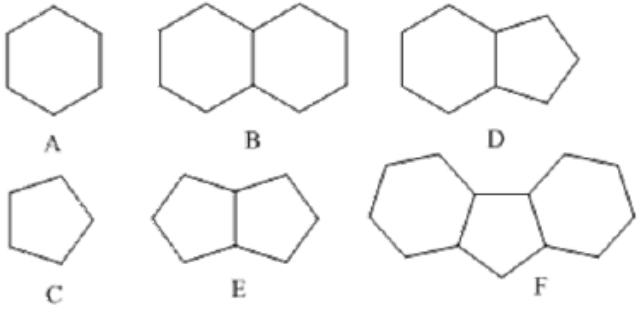
$$\Delta G_r = G_L + n/2\ G_{H_2O} - G_{LH_n} - n/4\ G_{O_2}$$

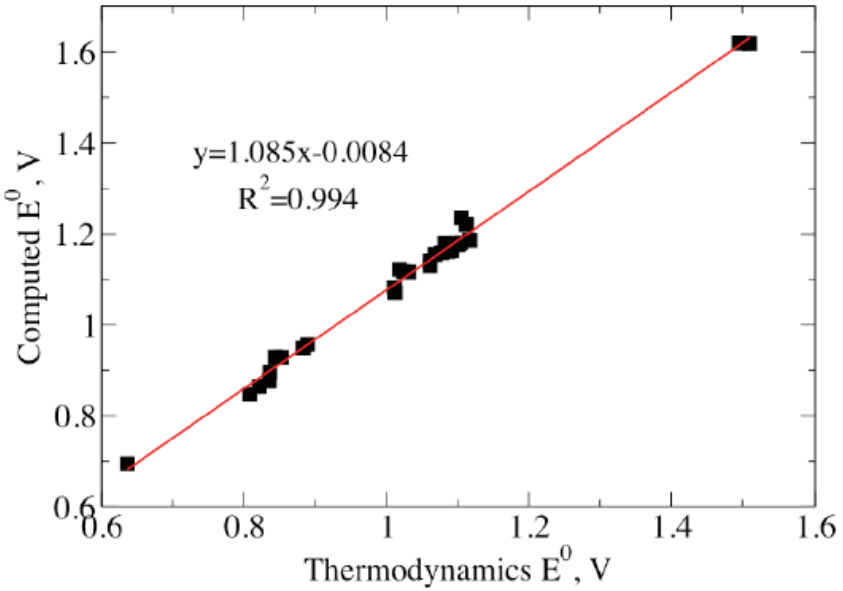
$$H = E_{elect} + U_{vib} + U_{trans} + U_{rot} + PV \qquad G = H - T(S_{vib} + S_{rot} + S_{trans})$$

$$H = H^0 + C_p(T - 298.15\ K) \qquad S = S^0 + C_p \ln(T/298.15\ K)$$

Fuel selection for regenerative organic fuel cell/flow battery: thermodynamic consideration, EES 5: 9534-9542 (2012)

C. Moyses Araujo, Davide L. Simone, Steven J. Konezny, Aaron Shim , Robert H. Crabtree, Grigorii L. Soloveichik, and Victor S. Batista





Correlation between OCP's obtained from the calculated free energies at B3LYP/cc-PVTZ theory level and from the experimental thermodynamic data (NIST database).

Calculated open circuit potentials and hydrogen gravimetric densities for six- (type A) and five-member (type C) ring fuels.

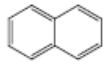
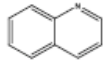
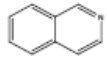
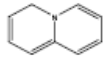
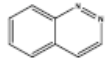
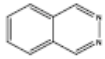
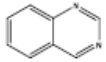
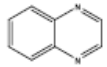
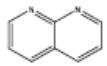
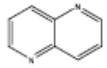
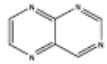
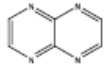
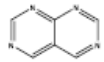
LOHC (in dehydrogenated state)		H, wt. %	E^0, V
Name	**Structure**		
Benzene		7.19	1.049
Pyridine		7.10	1.081
Pyrimidine		7.02	1.116
Pyridazine		7.02	1.085
1,3,5-triazine		6.94	1.198
Cyclopentadiene		5.75	0.854
Furan		5.59	1.004
1H-pyrrole		5.67	1.092
1H-imidazole		5.59	1.203
1H-pyrazole		5.59	1.269
1H-1,2,3-triazole		5.52	1.351
1H-1,2,4-triazole		5.52	1.328

Fuel selection for regenerative organic fuel cell/flow battery: thermodynamic consideration, EES 5: 9534-9542 (2012)

C. Moyses Araujo, Davide L. Simone, Steven J. Konezny, Aaron Shim ,
Robert H. Crabtree, Grigorii L. Soloveichik, and Victor S. Batista

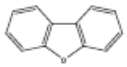
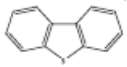
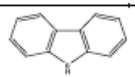
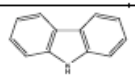
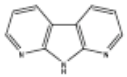
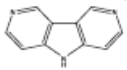
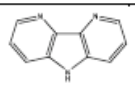
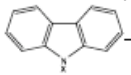
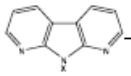
Calculated open circuit potentials and hydrogen gravimetric densities for fused six- (type D) and five-member (type E) ring fuels.

Organic carrier (in dehydrogenated state)		*H, wt. %*	*E^0, V*
Name	**Structure**		
1H-indene		6.49	1.041
benzofuran		6.39	1.084
benzo[b]thiophene		5.67	1.080
1H-indole		6.54	1.128
2H-isoindole		6.54	1.092
indolizine		6.54	1.064
1H-benzo [d]imidazole		6.49	1.187
1H-indazole		6.49	1.206
1H-pyrrolo [2,3-b]pyridine		6.39	1.167
imidazo[1,2-a] pyrazine		6.34	1.145
7H-purine		6.29	1.228
1,4-dihydropentalene		5.49	0.901
1H-pyrrolizine		5.44	1.017
1,4-dihydropyrrolo [3,2-b]pyrrole		5.39	1.159
1,4-dihydroimidazo [4,5-d]imidazole		5.30	1.313

Organic carrier (in dehydrogenated state)		*H, wt %*	*E^0, V*
Name	**Structure**		
naphthalene		7.29	1.078
quinoline		7.24	1.097
isoquinoline		**7.24**	1.098
4H-quinolizine		**5.79**	0.946
cinnoline		**7.19**	1.087
phthalazine		7.19	1.098
quinazoline		7.19	1.119
quinoxaline		7.19	1.108
1,8-naphthyridine		7.19	1.112
1,5-naphthyridine		7.19	1.115
pteridine		7.09	1.128
pyrazino[2,3-b] pyrazine		7.09	1.122
pyrimido[4,5-d] pyrimidine		7.09	1.160

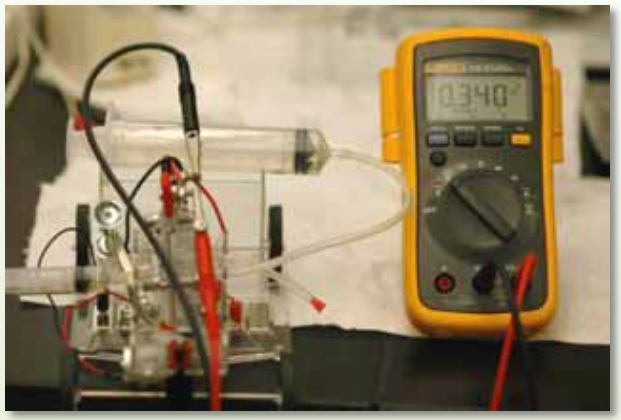
Fuel selection for regenerative organic fuel cell/flow battery: thermodynamic consideration, EES 5: 9534-9542 (2012)

C. Moyses Araujo, Davide L. Simone, Steven J. Konezny, Aaron Shim , Robert H. Crabtree, Grigorii L. Soloveichik, and Victor S. Batista

Organic carrier (in dehydrogenated state)		*H, wt %*	*E^0, V*
Name	**Structure**		
9H-fluorene		6.78	1.109
dibenzo[b,d]furan		6.71	1.125
dibenzo[b,d] thiophene		6.16	1.117
5H-dibenzo [b,d]borole		6.81	1.108
9H-carbazole		6.75	1.152
9H-pyrrolo [2,3-b:5,4-b'] dipyridine		6.67	1.206
5H-pyrrolo [3,2-c:4,5-c'] dipyridine		6.67	1.191
5H-pyrrolo [3,2-b:4,5-b'] dipyridine		6.67	1.181
9X-carbazole		H 6.75	1.152
		Et	1.167
9X-1,8-diazacarbazole		H 6.67	1.206
		Me	1.222
		Et	1.230

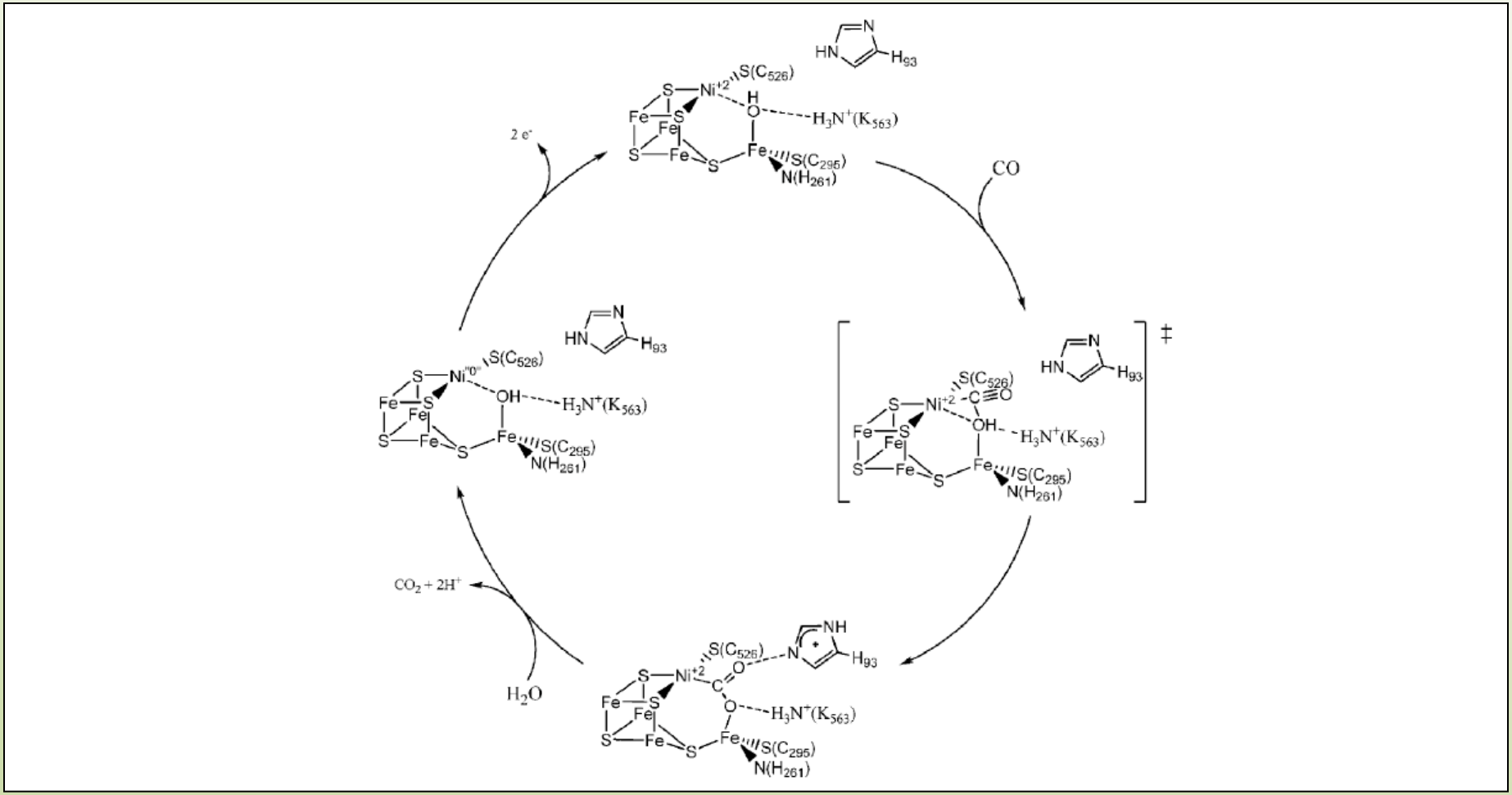
Boiling point, specific energy and energy density of selected organic fuels, and theoretical efficiency of fuel cells based on dehydrogenation.

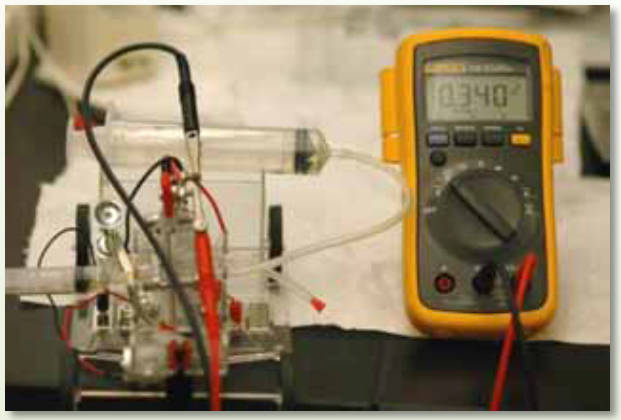
Organic carrier (in hydrogenated state)	Boiling point, °C	Specific energy, Wh/kg	Energy density, Wh/L	Efficiency, %
Liquid hydrogen	-252.9	-	2539	83.0
Pyrrolidine	87	1660	1438	92.8
Tetrahydrofurane	66	1500	1334	93.4
Tetrahydrothiophene	119	1196	1195	93.5
Cyclohexane	80.7	2025	1578	94.1
Methylcyclohexane	101	1747	1345	94.3
Cyclohexylamine	134.5	1772	1532	95.2
Chlorocyclohexane	66	1403	1403	93.4
Cyclohexanol	160.8	1686	1622	93.0
Cyclohexanethiol	158	1292	1227	94.0
Piperidine	106	2046	1764	94.2
2-methylpiperidine	118	1776	1499	94.5
Piperazine	146	2055	2260	95.7
trans-Decalin	187	2095	1877	93.1



Modeling Systems for CO_2/CO Conversion

Lesson From CO Dehydrogenases

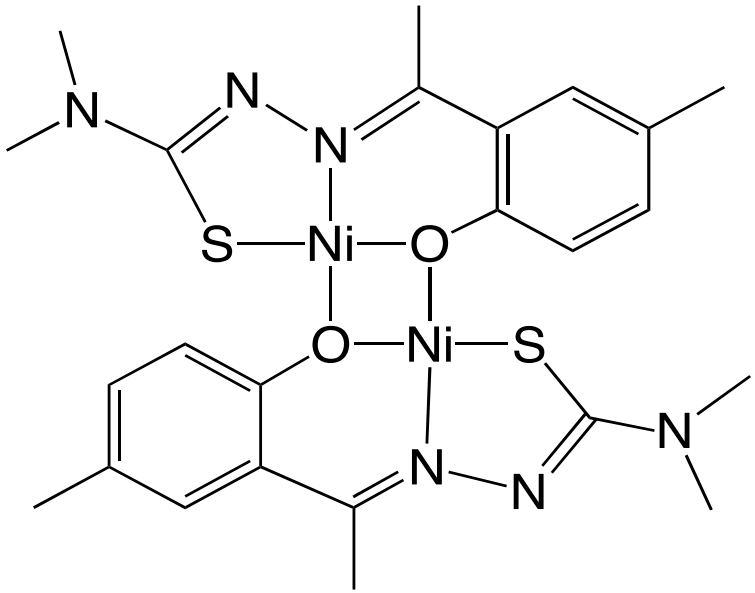




CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Systems for CO/CO_2 Conversion

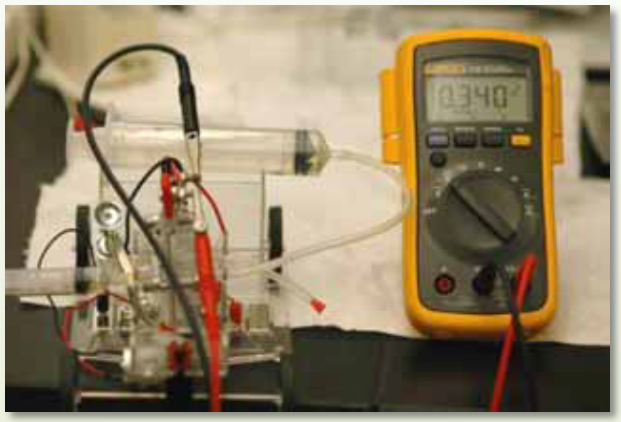
Crabtree's Biomimetic Ni Catalyst



1

$$CO + H_2O + 2AcO^- + 2mv^{2+} \rightleftharpoons CO_2 + 2AcOH + 2mv^+$$

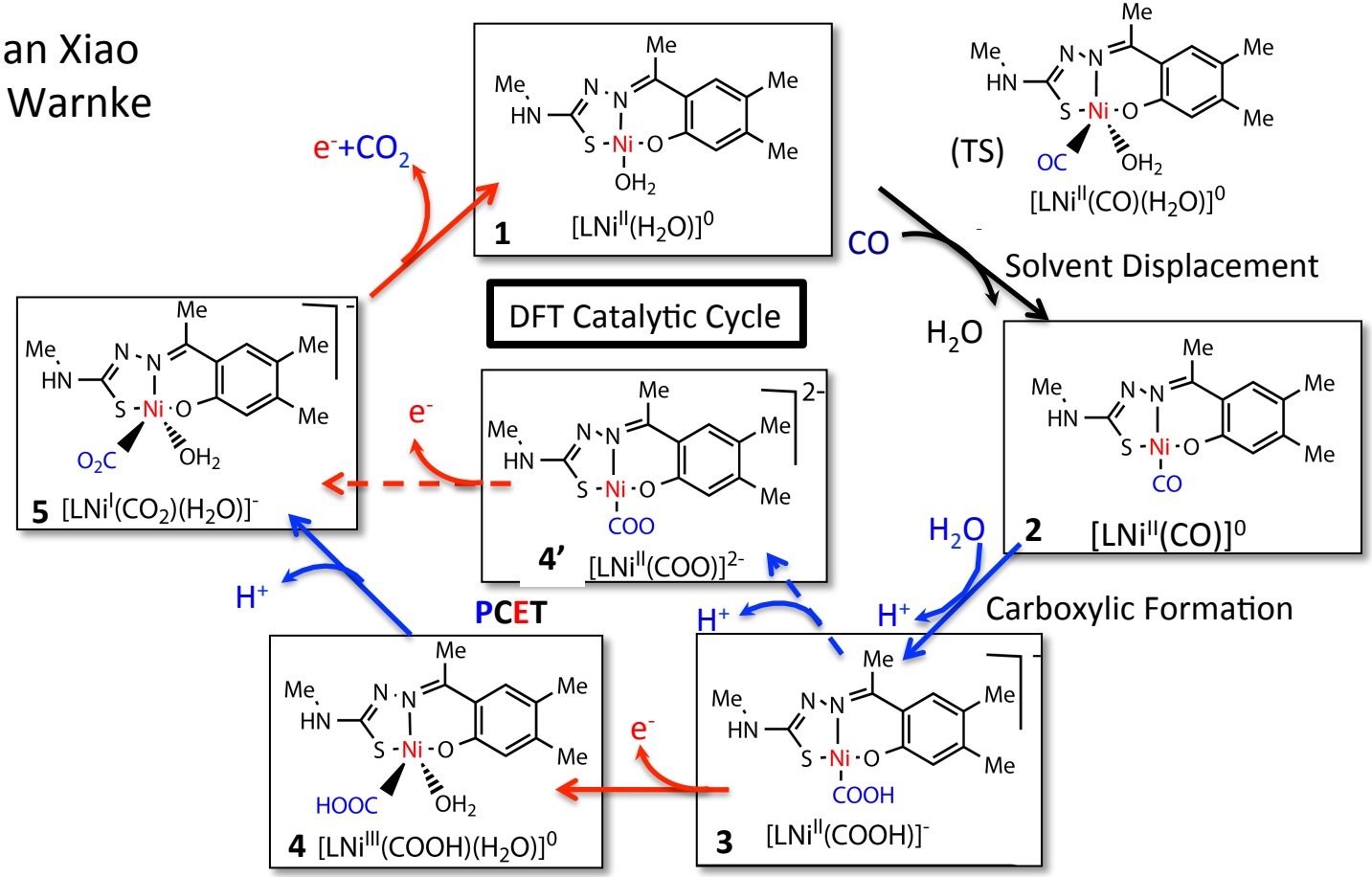
Lu, Z.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3994

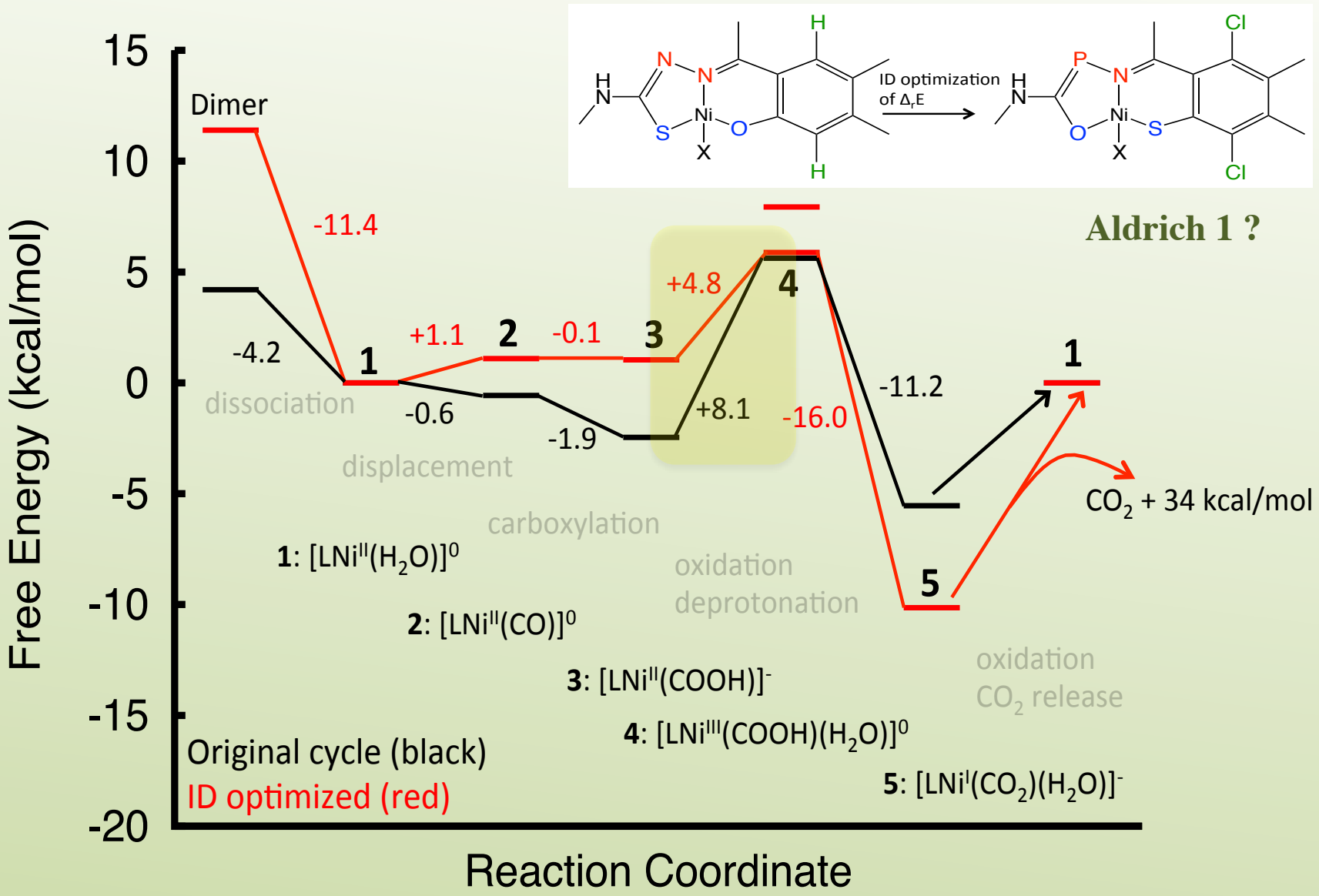


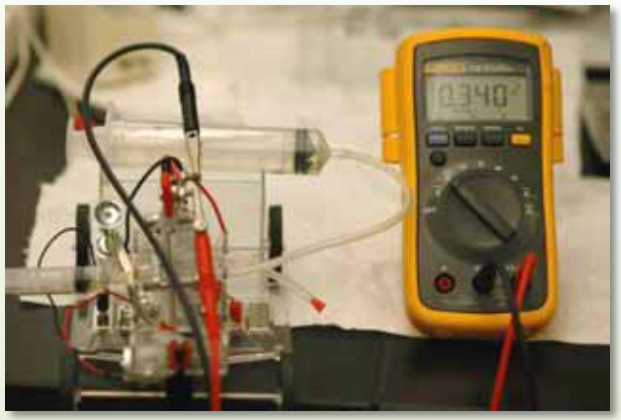
Inverse Design of Electrocatlysts: CO/CO_2 Conversion

Crabtree's Biomimetic Ni Catalyst

Dr. Dequan Xiao
Dr. Ingolf Warnke




15
10
5
0
-5
-10
-15
-20
Free Energy (kcal/mol)
Reaction Coordinate
Dimer
-11.4
-4.2
1
dissociation
+1.1
2
-0.1
3
displacement
-0.6
-1.9
+4.8
4
+8.1
-16.0
-11.2
1
carboxylation
oxidation
deprotonation
5
oxidation
CO2 release
CO2 + 34 kcal/mol
1: [LNiII(H2O)]0
2: [LNiII(CO)]0
3: [LNiII(COOH)]-
4: [LNiIII(COOH)(H2O)]0
5: [LNiI(CO2)(H2O)]-
Original cycle (black)
ID optimized (red)
ID optimization of ΔrE
Aldrich 1 ?



Modeling Systems for a Hydrogen Economy

CO Conversion into Liquid Fuel

The Fischer-Tropsch Process

1) Synthesis Gas Formation

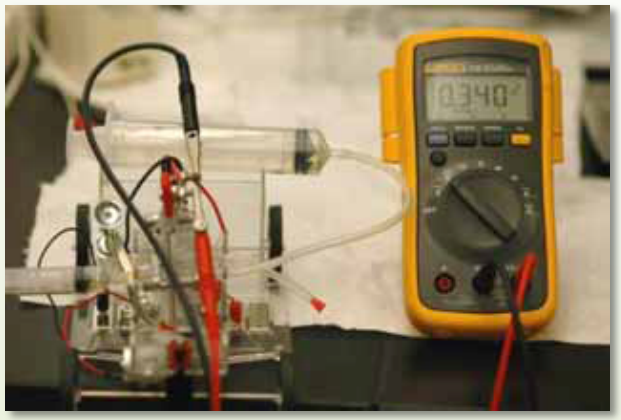
$$CH_n + O_2 \xrightarrow{\text{(Catalyst)}} \tfrac{1}{2}\, n\, H_2 + CO$$

2) Fischer-Tropsch Reaction

$$2n\, H_2 + CO \xrightarrow{\text{Catalyst}} -(CH_2-)_n- + H_2O$$

3) Refining

$$-(CH_2-)_n- \xrightarrow{\text{(Catalyst)}} \text{Fuels, lubricants, etc.}$$



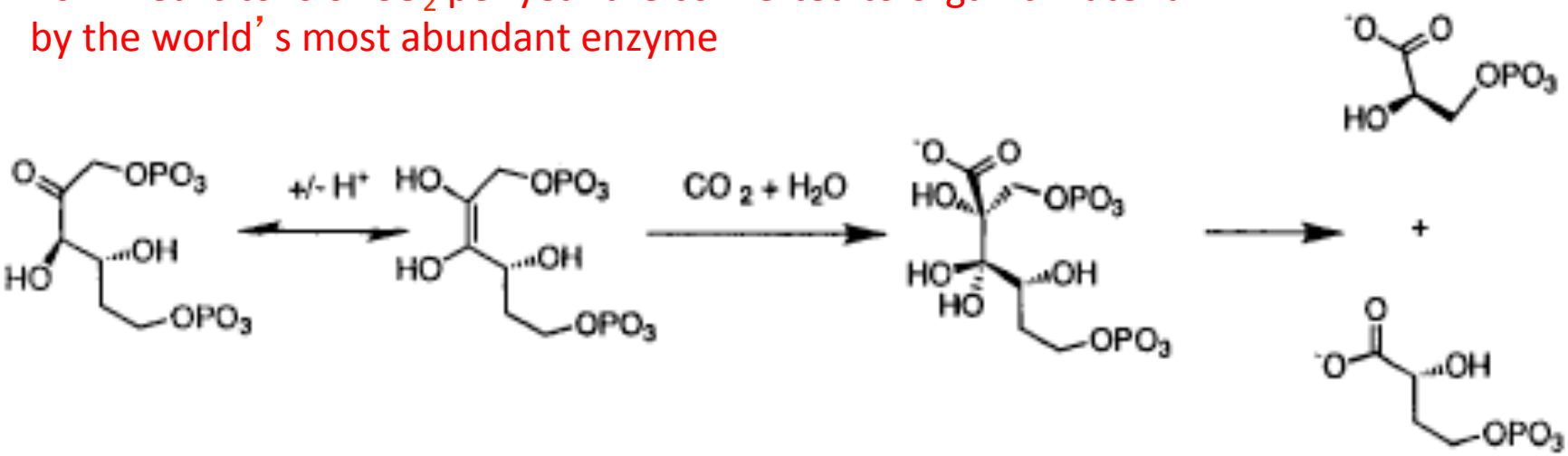
Modeling Systems for CO_2 Conversion

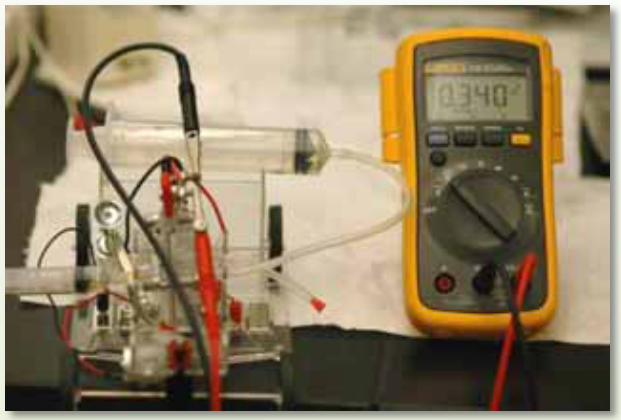
Lesson From Rubisco: CC Bond Formation

Natural CO_2 Fixation based on Mg Catalysts?

Carboxylation in Ribulose 1,5-BisPhosphate carboxylase (Rubisco)

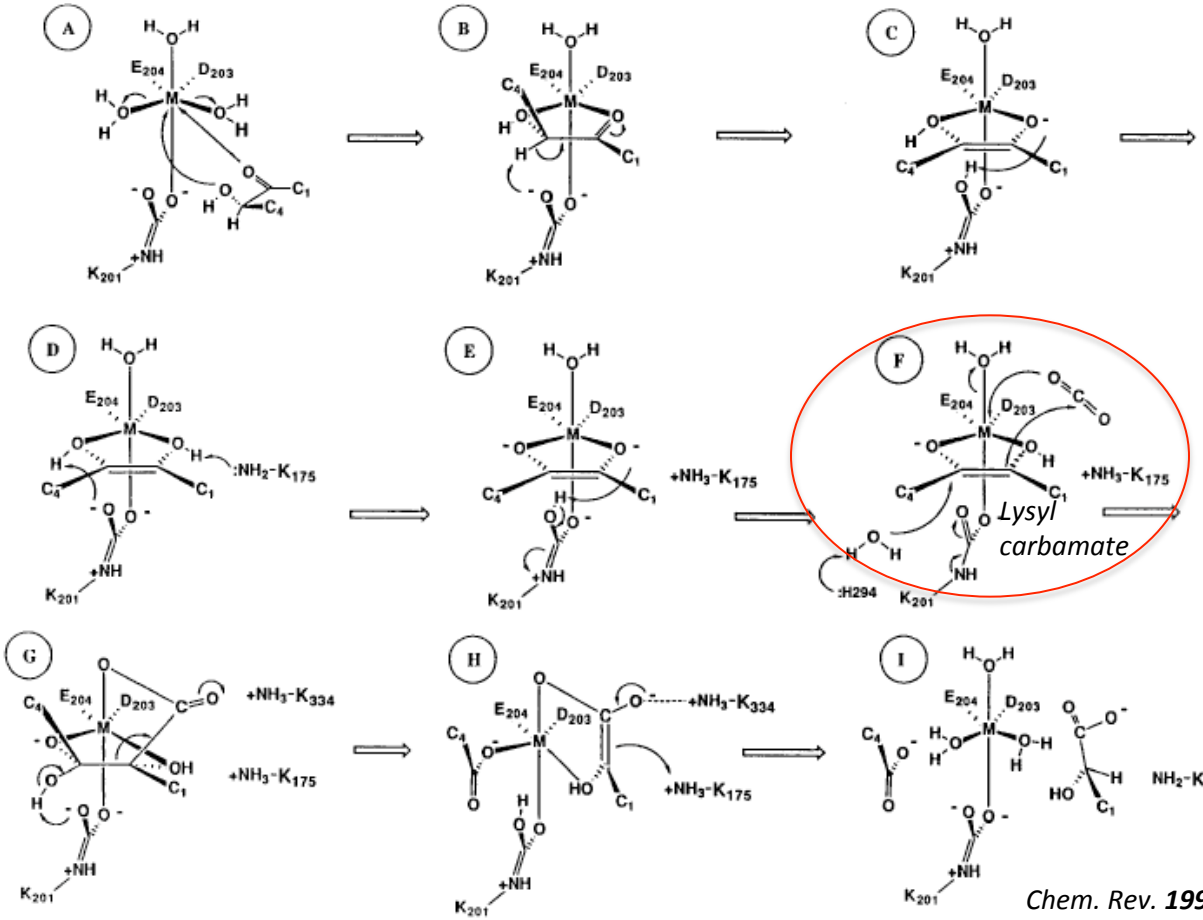
10^{11} metric tons of CO_2 per year are converted to organic material by the world's most abundant enzyme





Modeling Systems for CO_2 Conversion

Lesson From Rubisco: CC Bond Formation



Chem. Rev. ***1998, 98, 549-561***