2269-23

Workshop on New Materials for Renewable Energy

17 - 21 October 2011

Non-equilibrium dynamics of photoinduced proton-coupled electron transfer

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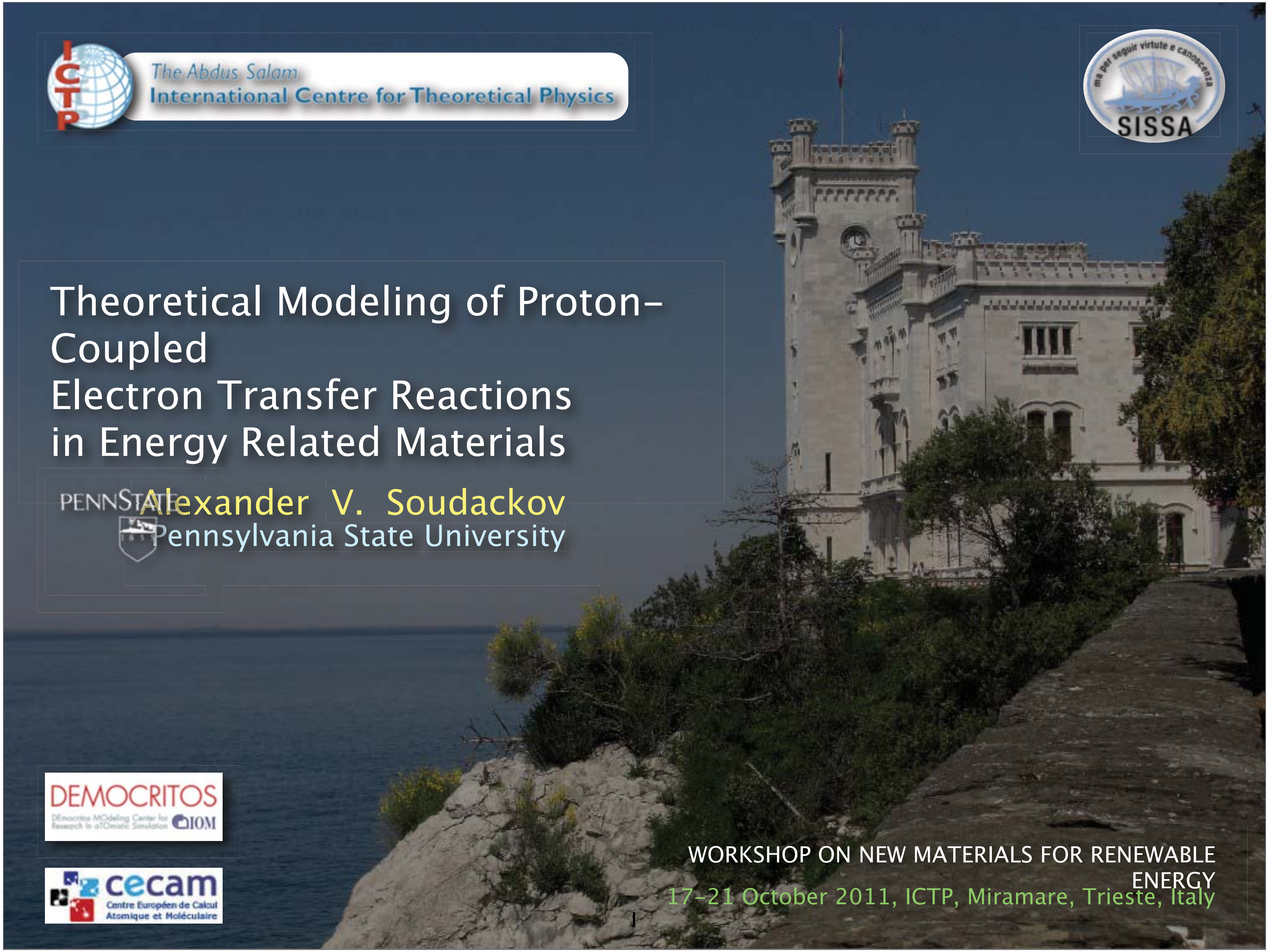
SISSA



Theoretical Modeling of Proton-Coupled Electron Transfer Reactions in Energy Related Materials

PENNSTATE

Alexander V. Soudackov
Pennsylvania State University

DEMOCRITOS
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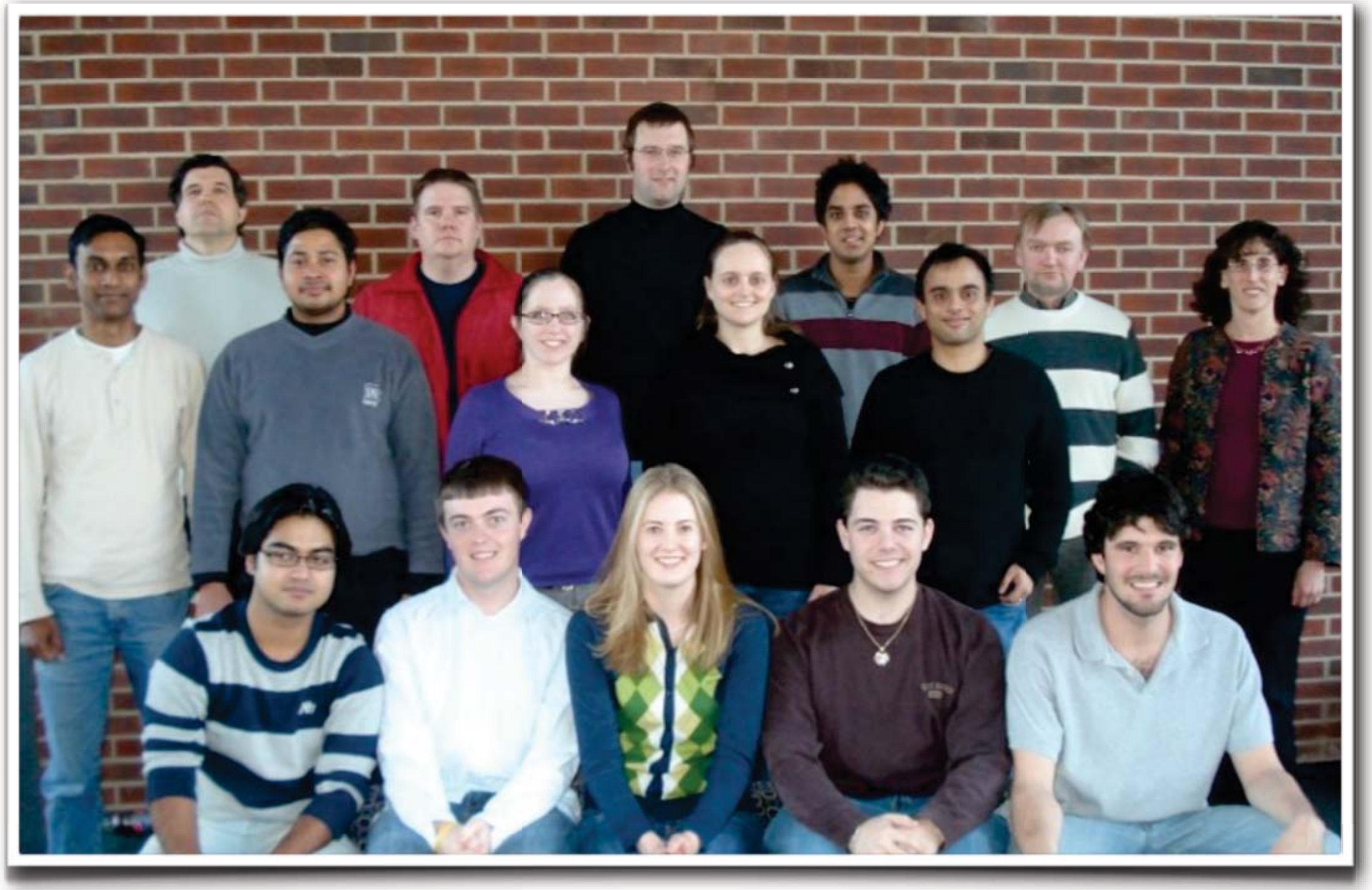
Centre Européen de Calcul Atomique et Moléculaire

WORKSHOP ON NEW MATERIALS FOR RENEWABLE ENERGY
17-21 October 2011, ICTP, Miramare, Trieste, Italy

Sharon Hammes-Sciffer (SHS) Group



Contributors

Sharon Hammes-Schiffer

Sarah Edwards
Model PCET studies

Michelle Ludlow
Os-complex on Gold electrode

Jonathan Skone
Electron-proton adiabaticity

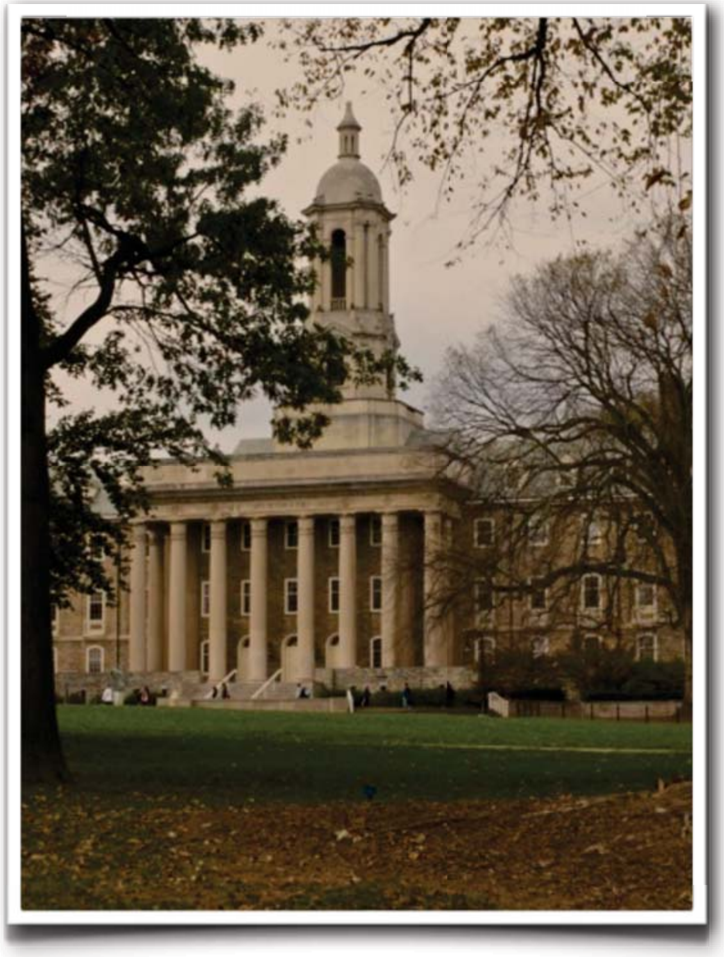
Liz Hatcher
PCET in lipoxygenase

Irina Navrotskaya
Anderson-Newns Hamiltonian for PCET

Charulatha Venkataraman
Interfacial PCET rate constants

Andrew Sirjoosingh
Diabatization methods in PCET

Random Facts about Penn State...



- **Largest* alumni base in the world**
  - Total Alumni: **557,331** (165,182 registered)
- **Notable alumni**
  - **Paul Berg** ’48, ’52g - Nobel Prize winner in Chemistry (1980): “for his fundamental studies of the biochemistry of nucleic acids, with particular regard to recombinant-DNA”
  - **Jef Raskin** ’67g - credited with being the father of the Macintosh computer

*unofficial and widely debated data

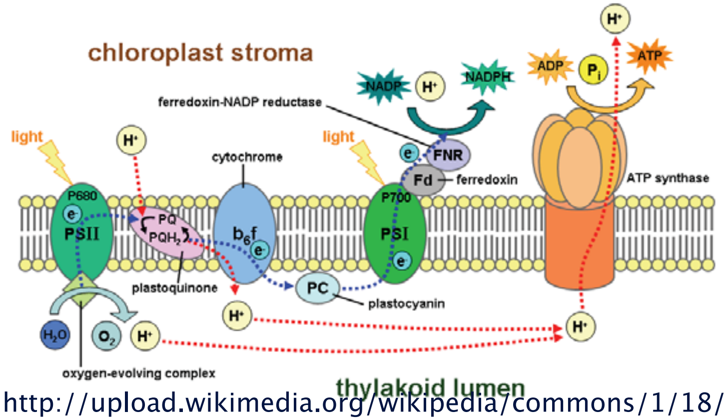
Outline

- Motivation and relevance
- General model for PCET
  - four-state model and reduced two-state model
  - vibronic free energy surfaces - generalized Marcus model
- Non-adiabatic PCET rate constant
  - Fermi Golden Rule formulation
  - Effects of proton donor-acceptor vibrational mode
- Free energy relationships and kinetic isotope effects
- Elecron-proton adiabaticity: HAT vs. PCET
- Electrochemical PCET
- Concluding remarks

Motivation

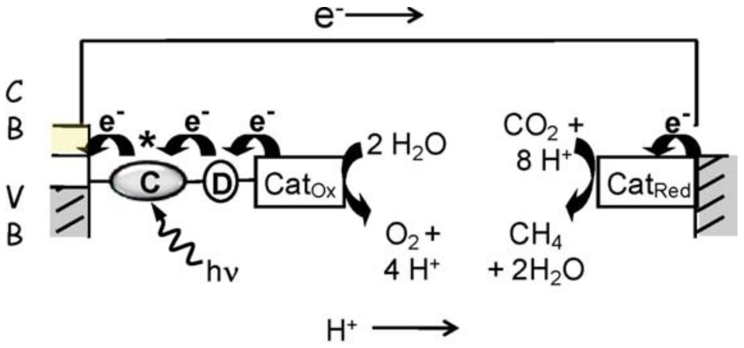
- PCET processes in energy related materials

Photosynthesis



http://upload.wikimedia.org/wikipedia/commons/1/18/Thylakoid_membrane.png

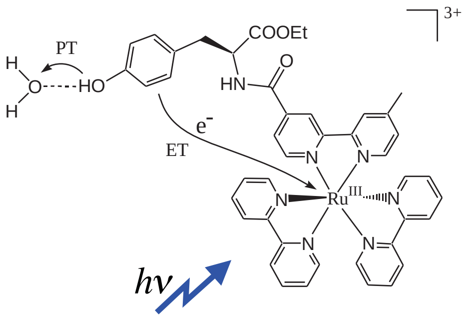
Dye sensitized photoelectrochemical cell

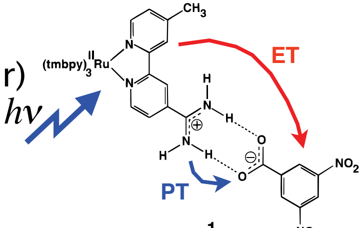


[Gagliardi et al., Coord. Chem. Rev., 254, 2459 (2010)]

Biomimetic systems

(Nocera, Hammarström, Meyer)





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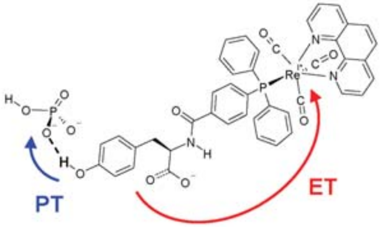
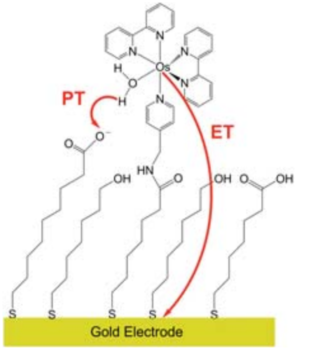


Electrochemical PCET

(Finklea)



$$\begin{tikzcd}
\mathrm{Os^{III}(OH)} + e^- \arrow[r, leftrightharpoons] \arrow[d, leftrightharpoons, "+\ H^+"'] \arrow[dr, leftrightarrow] & \mathrm{Os^{II}(OH)} \arrow[d, leftrightharpoons, "+\ H^+"] \\
\mathrm{Os^{III}(H_2O)} + e^- \arrow[r, leftrightharpoons] & \mathrm{Os^{II}(H_2O)}
\end{tikzcd}$$

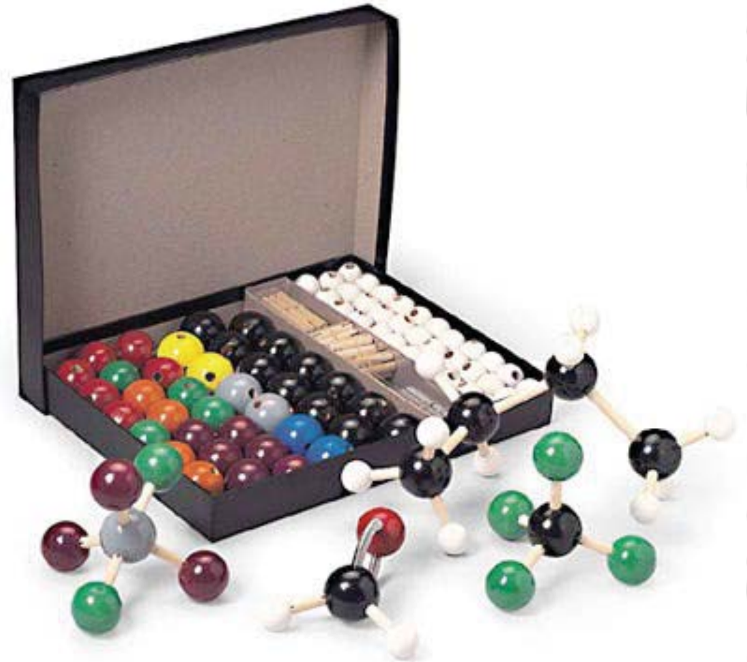
Questions

- key-factors/properties affecting the rates?
- can we predict the trends in rates and kinetic isotope effects?
- can we provide interpretations of experimental data?
- can theory provide insights into fundamental mechanism?
- can we calculate PCET rate constants from first principles?

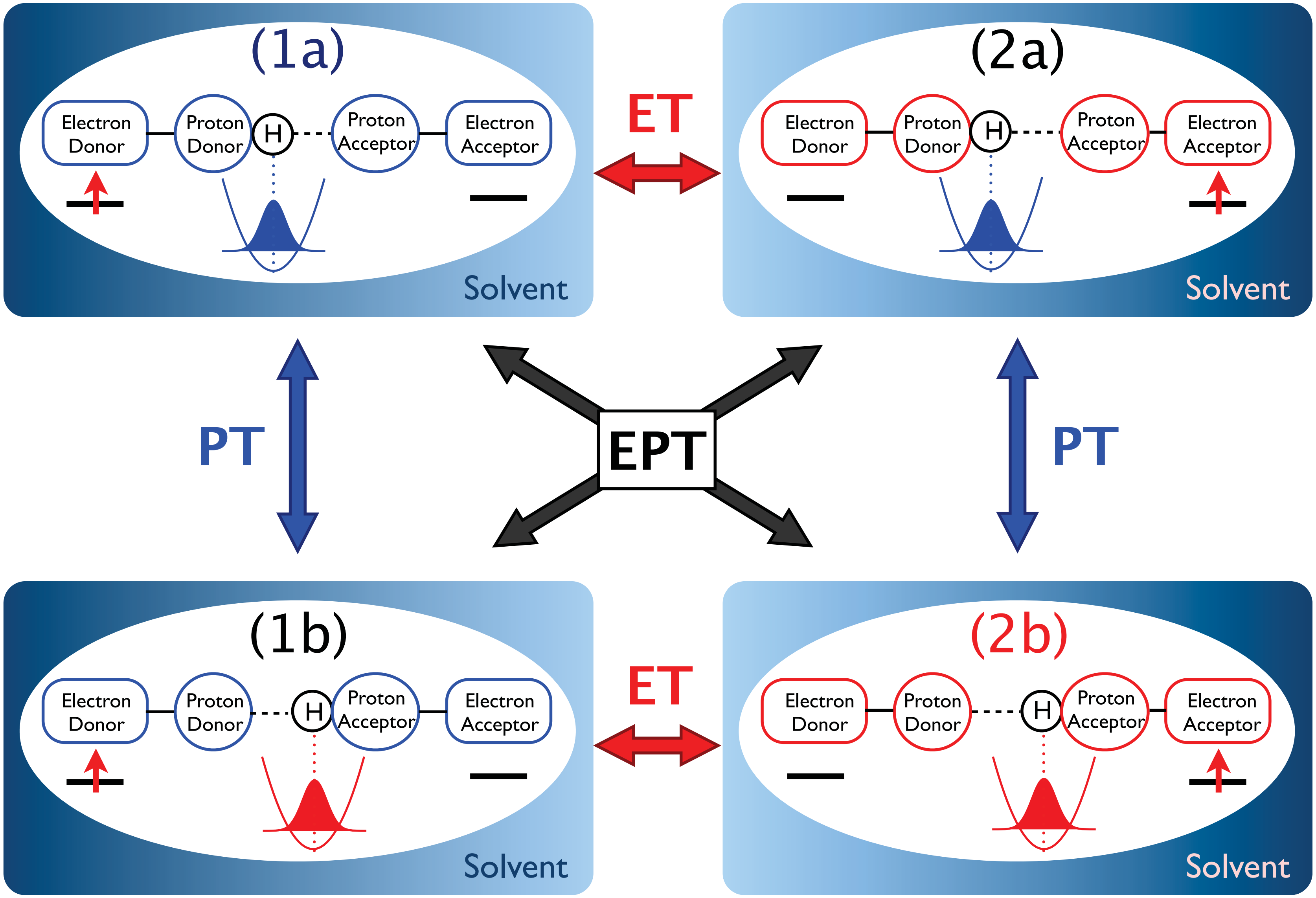
Questions

- key-factors/properties affecting the rates?
- can we predict the trends in rates and kinetic isotope effects?
- can we provide interpretations of experimental data?
- can theory provide insights into fundamental mechanism?
- can we calculate PCET rate constants from first principles?

General model for PCET



Four-state model for PCET



(1a)

Electron Donor — Proton Donor — H ··· Proton Acceptor — Electron Acceptor

Solvent

ET

(2a)

Electron Donor — Proton Donor — H ··· Proton Acceptor — Electron Acceptor

Solvent

PT

EPT

PT

(1b)

Electron Donor — Proton Donor ··· H — Proton Acceptor — Electron Acceptor

Solvent

ET

(2b)

Electron Donor — Proton Donor ··· H — Proton Acceptor — Electron Acceptor

Solvent

“2b, or not 2b: that is the

William Shakespear (1564-1616)

Hamlet, Act III, Scene 1

Four-state model for PCET

Gas phase vibronic Hamiltonian

$$H_0 = T_p + \begin{pmatrix} U_{1a}(r_p) & V^{PT} & V^{ET} & V^{EPT} \\ V^{PT} & U_{1b}(r_p) & V^{EPT} & V^{ET} \\ V^{ET} & V^{EPT} & U_{2a}(r_p) & V^{PT} \\ V^{EPT} & V^{ET} & V^{PT} & U_{2b}(r_p) \end{pmatrix}$$

Vibronic states are obtained by diagonalizing the Hamiltonian
in the appropriate electron-proton vibronic basis

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Four-state model for PCET

Vibronic Hamiltonian including interaction with the solvent

$$\bar{H} = T_p + \begin{bmatrix} U_{1a}(r_p) & V^{\mathrm{PT}} & V^{\mathrm{ET}} & V^{\mathrm{EPT}} \\ V^{\mathrm{PT}} & U_{1b}(r_p) + z_{\mathrm{p}} & V^{\mathrm{EPT}} & V^{\mathrm{ET}} \\ V^{\mathrm{ET}} & V^{\mathrm{EPT}} & U_{2a}(r_p) + z_{\mathrm{e}} & V^{\mathrm{PT}} \\ V^{\mathrm{EPT}} & V^{\mathrm{ET}} & V^{\mathrm{PT}} & U_{2b}(r_p) + z_{\mathrm{p}} + z_{\mathrm{e}} \end{bmatrix}$$

Vibronic states are obtained by diagonalizing the Hamiltonian
in the appropriate electron-proton vibronic basis

Four-state model for PCET

ET-blocks of the vibronic Hamiltonian

$$V^{ET}, V^{EPT} = V^{PT}$$

$$\bar{H} = T_p + \begin{pmatrix} U_{1a}(r_p) & V^{PT} & V^{ET} & V^{EPT} \\ V^{PT} & U_{1b}(r_p) + z_p & V^{EPT} & V^{ET} \\ V^{ET} & V^{EPT} & U_{2a}(r_p) + z_e & V^{PT} \\ V^{EPT} & V^{ET} & V^{PT} & U_{2b}(r_p) + z_p + z_e \end{pmatrix}$$

Vibronic states are obtained by diagonalizing the Hamiltonian
in the appropriate electron-proton vibronic basis

Reduction to two-state model

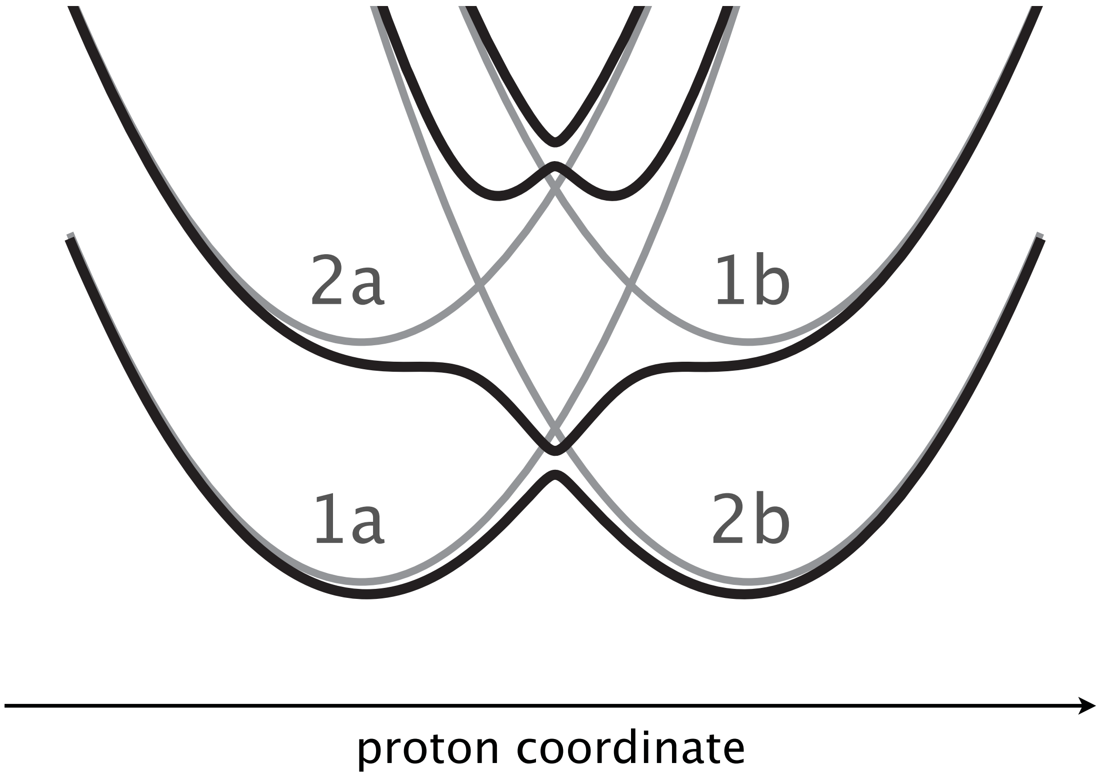
Vibronic Hamiltonian with interaction
for reduced two-state model

$$H_0 = T_p + \begin{pmatrix} U_I(r_p, z_p) & V^{el} \\ V^{el} & U_{II}(r_p, z_p, z_e) \end{pmatrix}$$

Vibronic states are obtained by diagonalizing the Hamiltonian
in the appropriate electron-proton vibronic basis

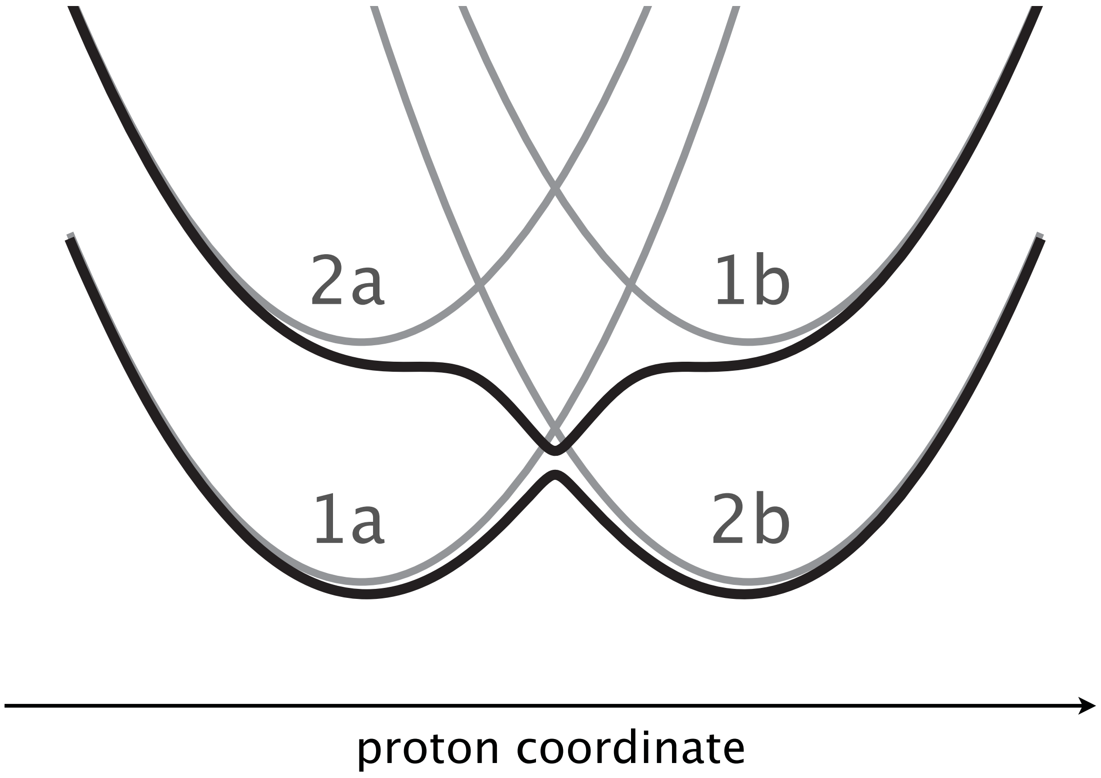
Reduction to two-state model

4 states: 1a, 1b, 2a, 2b



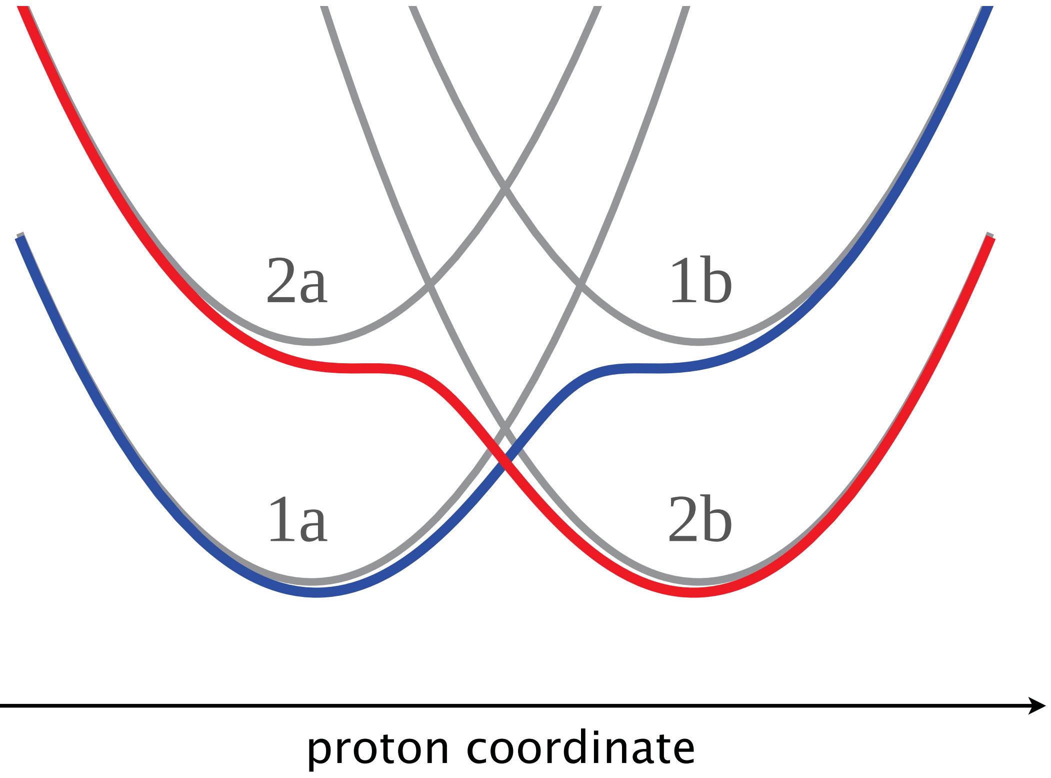
Reduction to two-state model

4 states: 1a, 1b, 2a, 2b



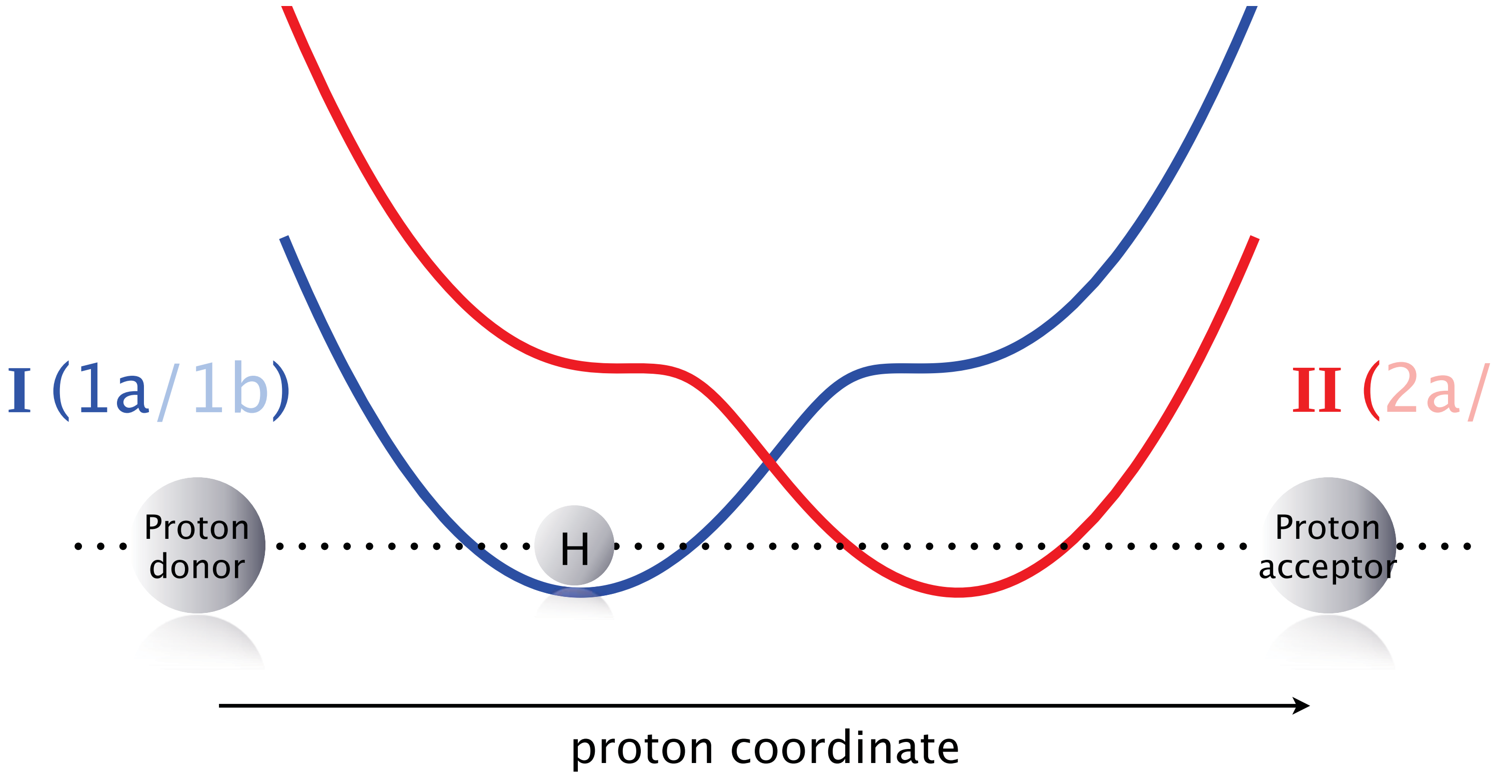
Reduction to two-state model

two ET blocks: 1a/1b and 2a/2b



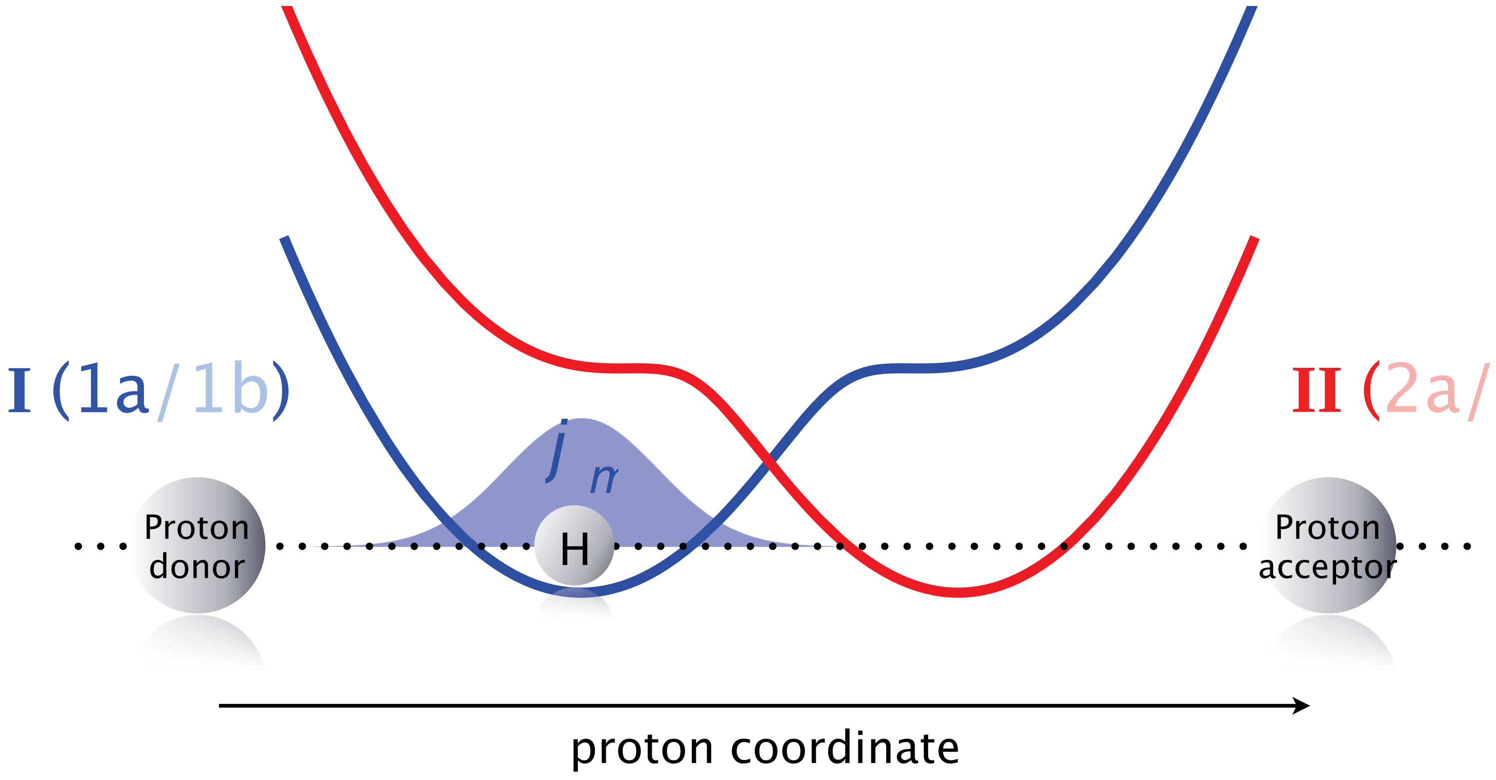
Reduction to two-state model

two states: lowest 1a/1b and lowest 2a/2b



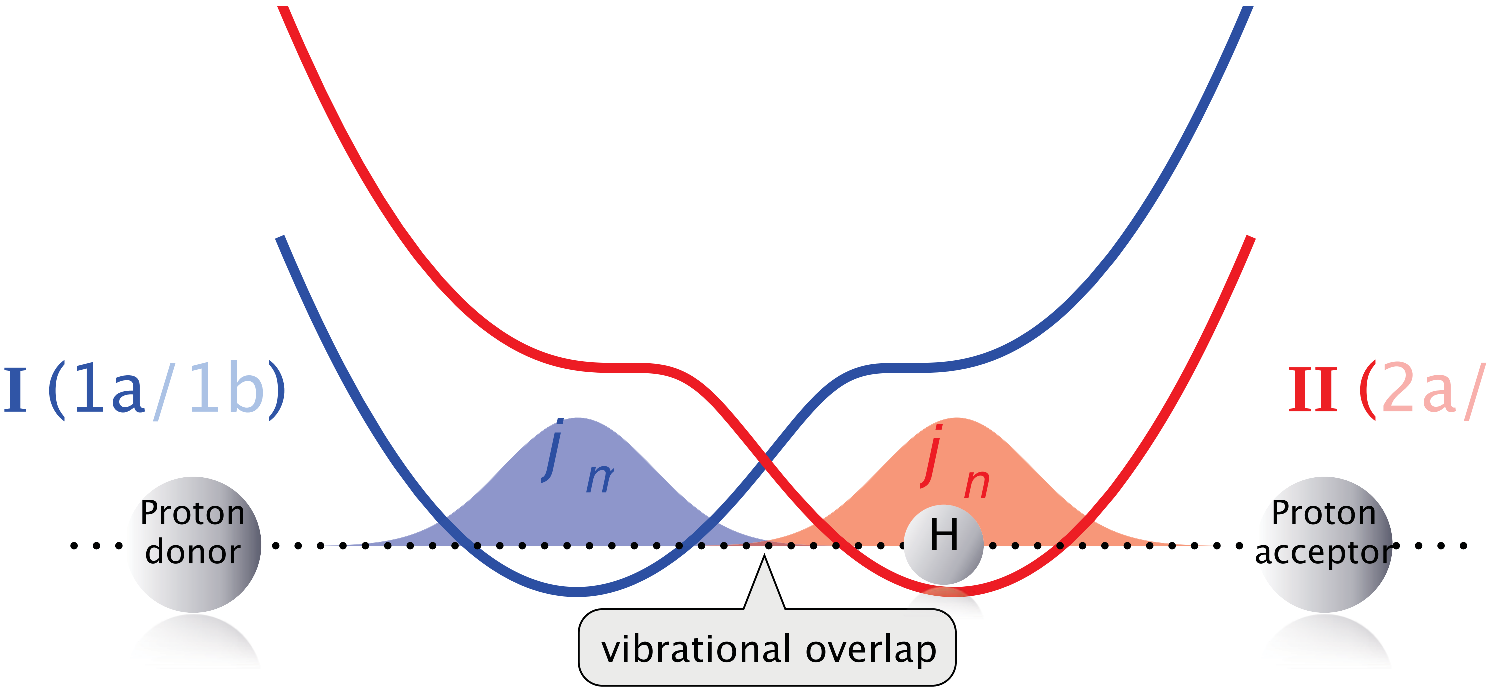
Reduction to two-state model

two states: lowest 1a/1b and lowest 2a/2b



Reduction to two-state model

two states: lowest 1a/1b and lowest 2a/2b

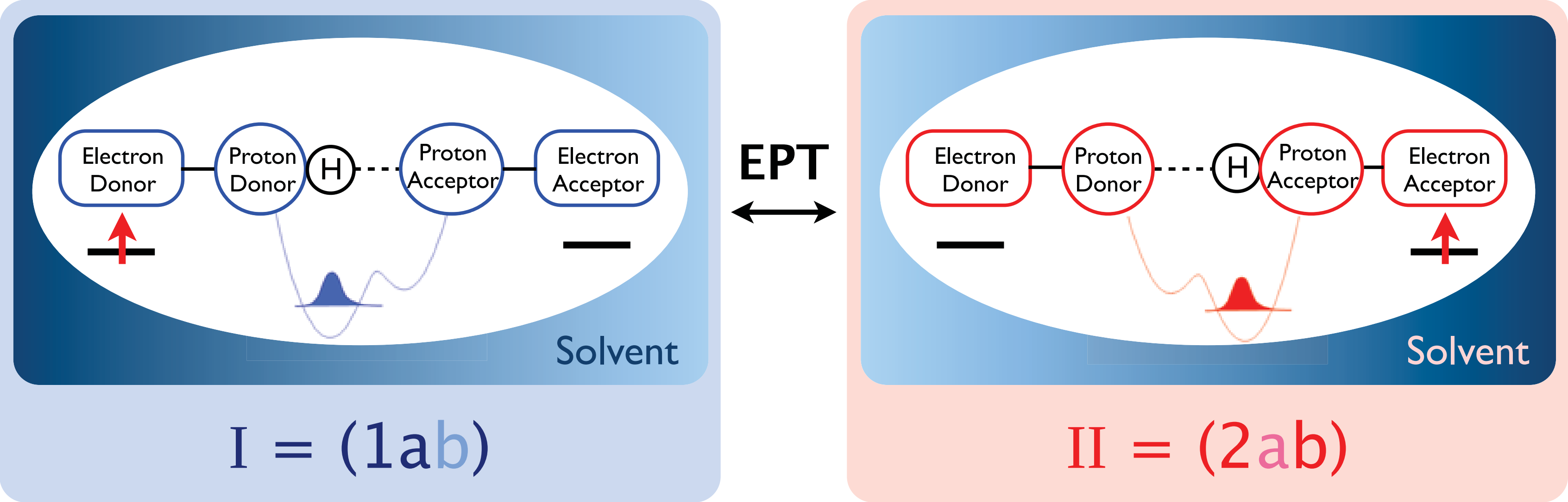


proton coordinate

$$V_{mn} = \langle \mathrm{I}\,m | \hat{H} | \mathrm{II}\,n \rangle \approx V^{el} S_{mn}$$

Two-state model for concerted PCET

- limited to strong hydrogen bonds with highly asymmetric proton potentials



- thermal reactions for majority of PCET systems exhibiting concerted EPT can be described in the framework of the two-state model
- non-equilibrium (photoinduced) PCET may require four-state model to properly describe proton vibrational relaxation

Interaction with polar solvent

Vibronic free energy surfaces

- Generalized Marcus model (in terms of energy gap coordinate)
  - solvent degrees of freedom adiabatically separated
  - linear response approximation: quadratic dependence of self energy
  - electron-proton vibronic Hamiltonian and its eigenstates parametrically depend on energy gap coordinate(s)

$$\mathrm{U}_n(z_\mathrm{p}, z_\mathrm{e}) = S(z_\mathrm{p}, z_\mathrm{e}) + W_n(z_\mathrm{p}, z_\mathrm{e})$$

free energy of
n-th vibronic state

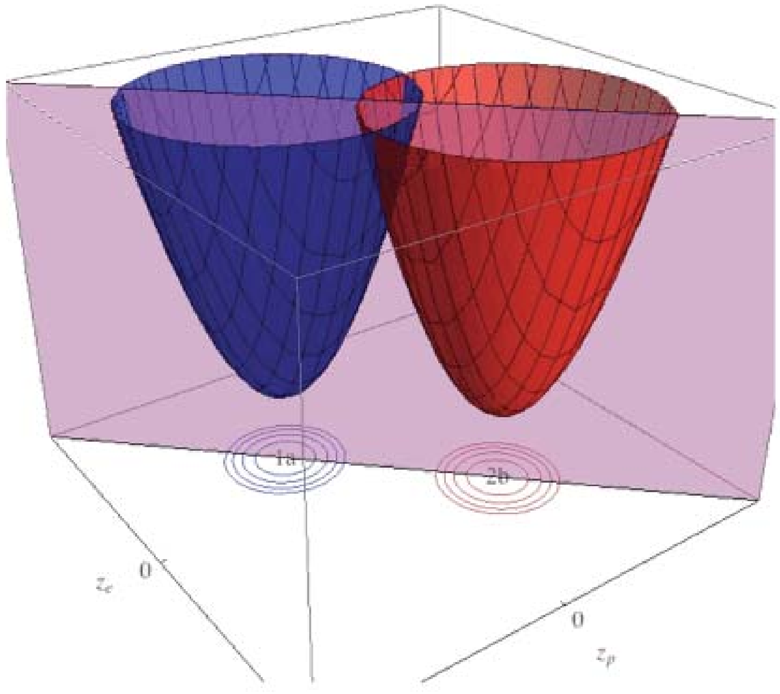
quadratic self energy of
solvent-solvent interactions
(depends on reorganization energies)

vibronic energy including
solute-solvent interaction

[Basilevsky, Chudinov, Newton, 1994; Soudackov, Hammes-Schiffer, 1999]

Interaction with polar solvent

Vibronic free energy surfaces

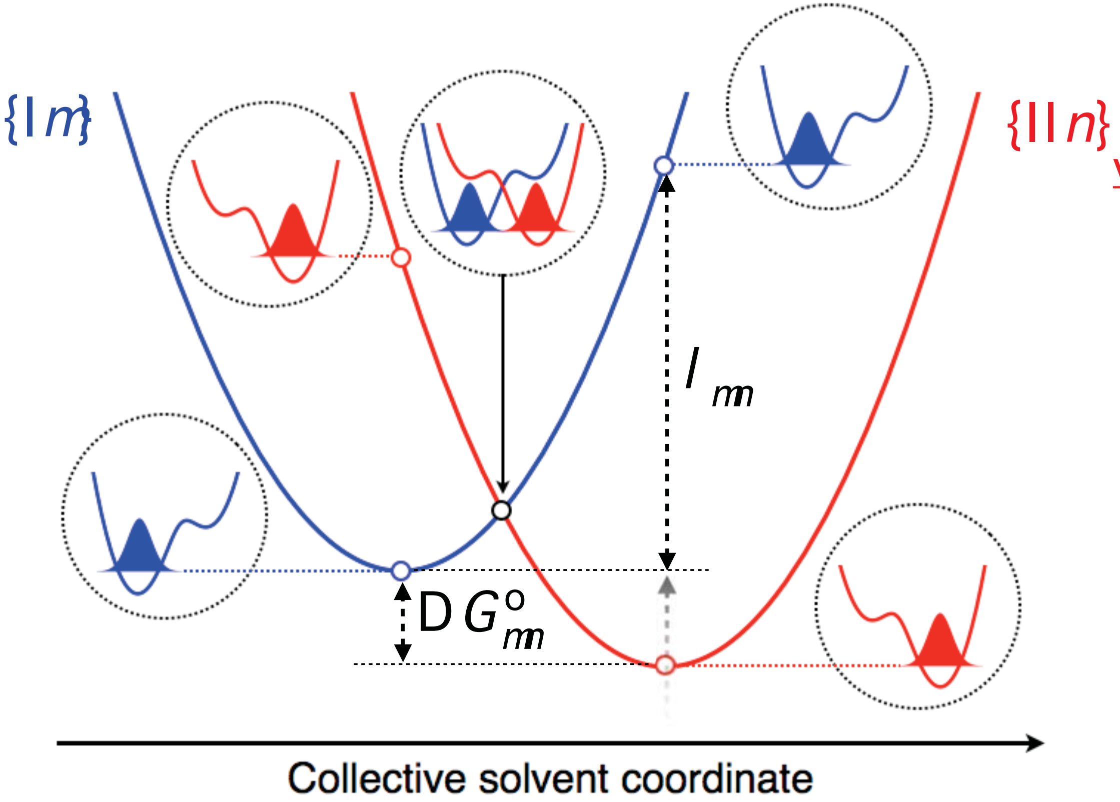


$$U_n(z_p, z_e) = S(z_p, z_e) + W_n(z_p, z_e)$$

[Basilevsky, Chudinov, Newton, 1994; Soudackov, Hammes-Schiffer, 1999]

Marcus picture (vibronic model)

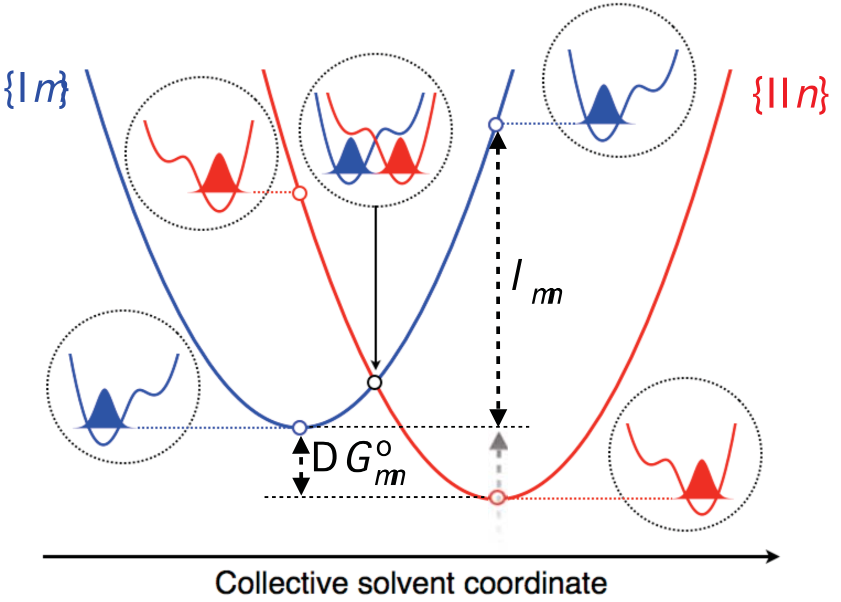
reactant
vibronic states



product
vibronic states

Marcus picture (vibronic model)

reactant
vibronic states



product
vibronic states

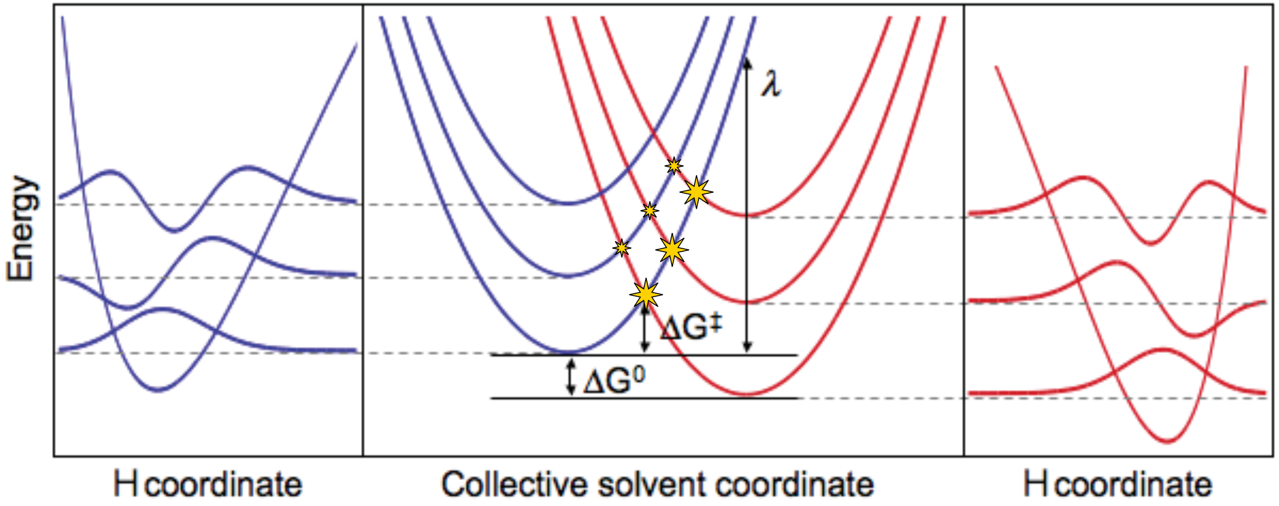
Nonadiabatic (Golden rule) rate expression

$$k^{\mathrm{PCET}} = \frac{2\pi}{\hbar}\sum_{\mu}\rho_{I\mu}\sum_{\nu}\left(4\pi\lambda_{\mu\nu}k_BT\right)^{-1/2}\left|V_{\mu\nu}\right|^2\exp\left[-\Delta G^{\ddagger}_{\mu\nu}/(k_BT)\right]$$

$$\Delta G^{\ddagger}_{\mu\nu} = \frac{(\Delta G^{\circ}_{\mu\nu}+\lambda_{\mu\nu})^2}{4\lambda_{\mu\nu}}; \qquad V_{\mu\nu} = \langle I\mu|\hat{H}|II\nu\rangle \approx V^{el}S_{\mu\nu}$$

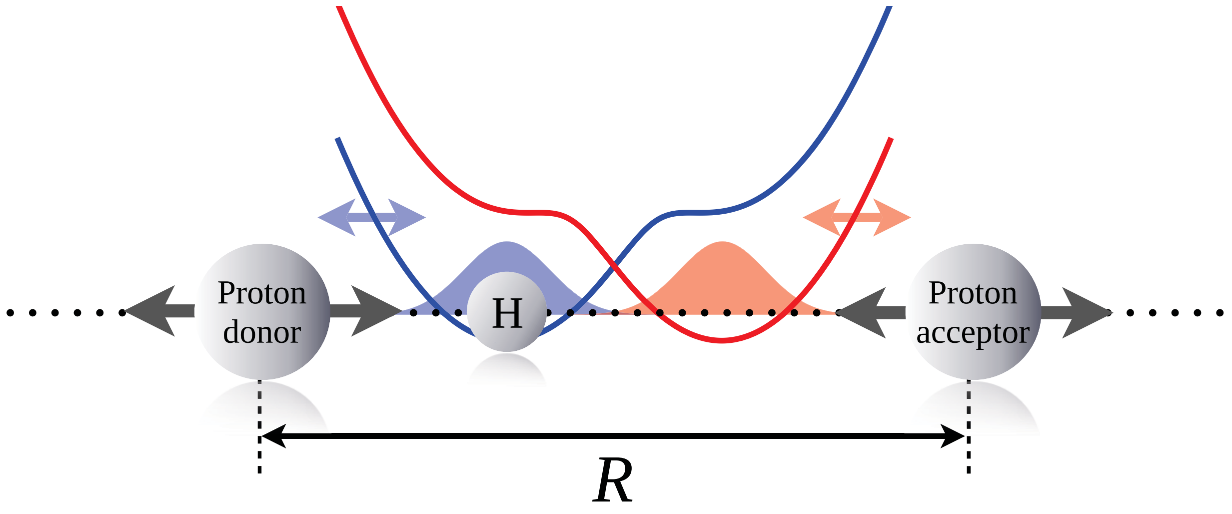
[Soudackov and Hammes-Schiffer: J. Chem. Phys. 2000]

Contributions of excited vibronic states



- Factors affecting relative contributions:
    - Boltzmann populations of reactant states
    - Free energy barriers
    - Vibronic couplings (proton vibrational overlaps)

Effects of proton donor–acceptor vibrational



- Vibronic coupling (and overlap) depends strongly on R – can be approximated as a single exponential (Taylor expansion of the logarithm):

$$V_{\mu\nu} \approx V^0_{\mu\nu} \exp\left[-\alpha_{\mu\nu}\left(R - R_0\right)\right] \qquad V^0_{\mu\nu} \approx V^{\mathrm{el}} S_{\mu\nu}(R_0)$$

[Soudackov, Hatcher, and Hammes-Schiffer: J. Chem. Phys. 2005]

Effects of proton donor-acceptor vibrational

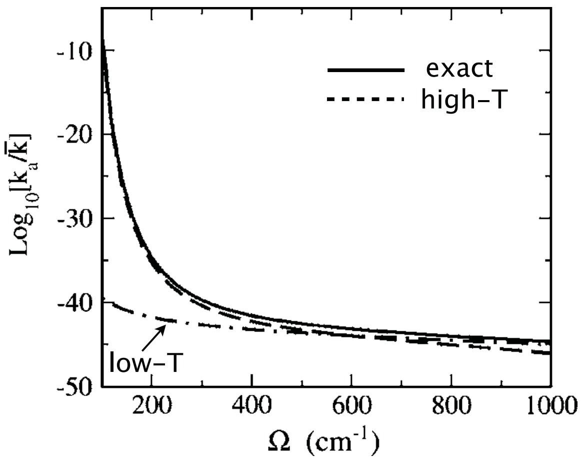
$$\Lambda_{\mu\nu} = \lambda_s + \lambda_R + \lambda^{(\alpha)}_{\mu\nu}; \qquad \lambda_R = \frac{1}{2}M\Omega^2\delta R^2; \qquad \lambda^{(\alpha)}_{\mu\nu} = \frac{\hbar^2\alpha^2_{\mu\nu}}{2M}$$

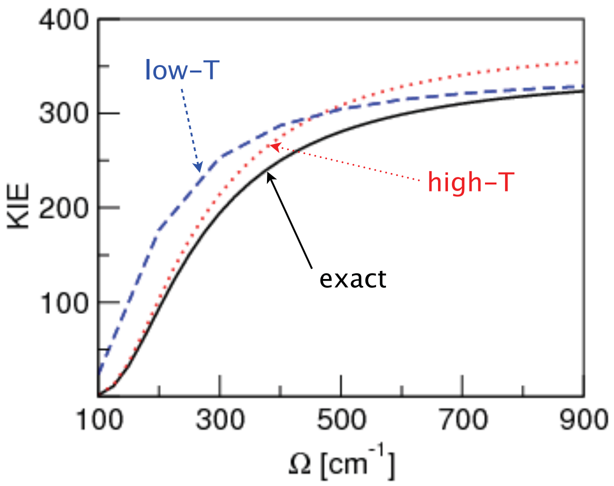
High-temperature (low frequency) limit: $(\hbar\Omega \ll k_{\mathrm{B}}T)$

$$k^{\mathrm{PCET}} = \frac{2\pi}{\hbar}\sum_{\mu} P_{I\mu}\sum_{\nu}\left(4\pi\Lambda_{\mu\nu}k_{\mathrm{B}}T\right)^{-1/2}\left|V_{\mu\nu}(R_0)\right|^2 \exp\left[\frac{2\alpha_{\mu\nu}k_{\mathrm{B}}T}{M\Omega^2}\right]\exp\left[-\frac{\left(\Delta G^0_{\mu\nu} + \Lambda_{\mu\nu} + 2\alpha_{\mu\nu}\delta R k_{\mathrm{B}}T\right)}{4\Lambda_{\mu\nu}k_{\mathrm{B}}T}\right]$$

Low-temperature (high frequency) limit: $(\hbar\Omega \gg k_{\mathrm{B}}T)$

$$k^{\mathrm{PCET}} = \frac{2\pi}{\hbar}\sum_{\mu} P_{I\mu}\sum_{\nu}\left(4\pi\lambda_s k_{\mathrm{B}}T\right)^{-1/2}\left|V_{\mu\nu}(R_0)\right|^2 \exp\left[\frac{\lambda^{(\alpha)}_{\mu\nu} - \lambda_R}{\hbar\Omega} - \alpha_{\mu\nu}\delta R\right]\exp\left[-\frac{\left(\Delta G^0_{\mu\nu} + \lambda_s\right)}{4\lambda_s k_{\mathrm{B}}T}\right]$$

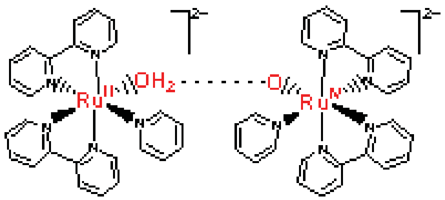


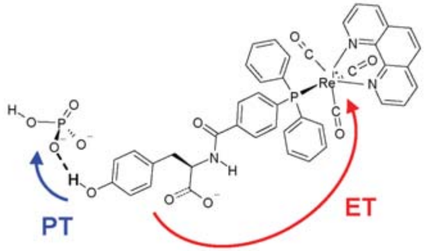


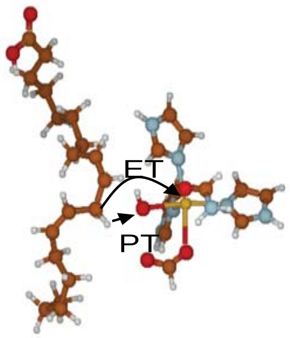
[Soudackov, Hatcher, and Hammes-Schiffer: J. Chem. Phys. 2005]

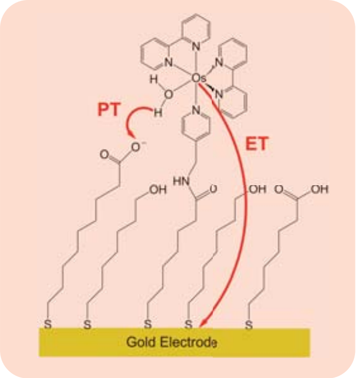
Applications

System	Experiment	Theory
Amidinium-carboxylate salt bridges	Nocera	JACS 1999
Iron bi-imidazoline complexes	Mayer/Roth	JACS 2001
Ruthenium polypyridyl complexes	Meyer/Thorp	JACS 2002
DNA-acrylamide complexes	Sevilla	JPCB 2002
Ruthenium-tyrosine complex	Hammarström	JACS 2003
Soybean lipoxygenase enzyme	Klinman	JACS 2004,
Rhenium-tyrosine complex	Nocera	JACS 2007
Quinol oxidation	Kramer	JACS 2009
Osmium aquo complex/SAM/gold	Finklea	JACS 2010



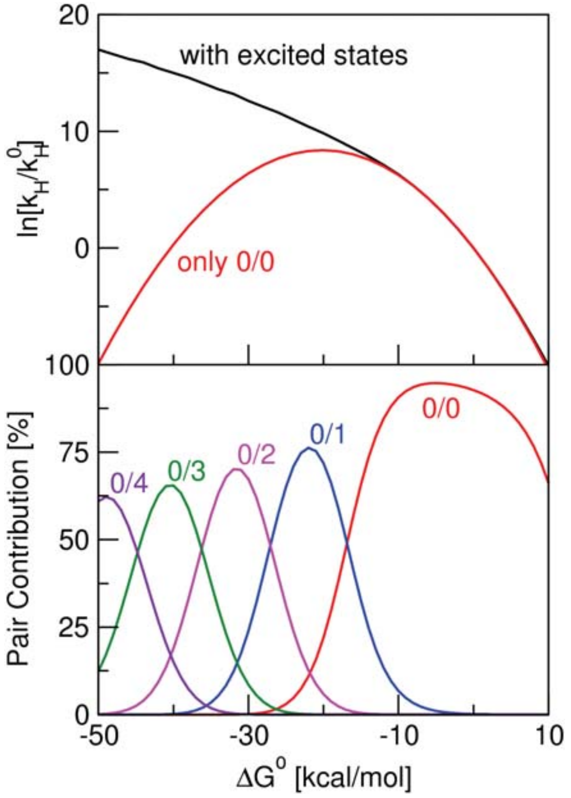


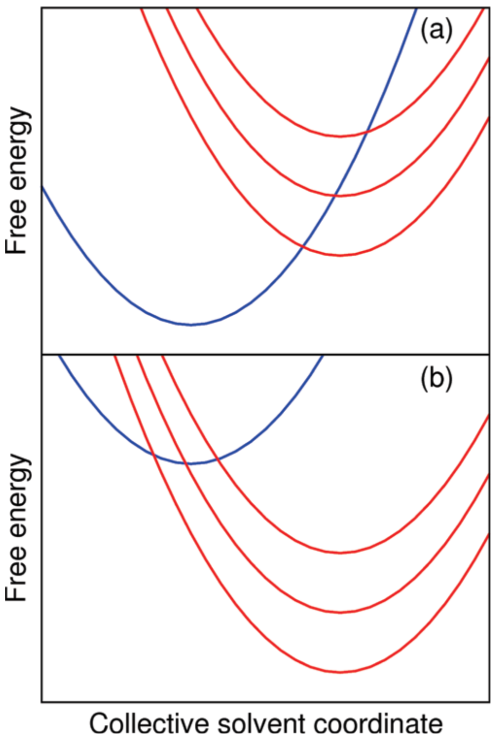




Free energy relationship for PCET

Excited vibrational states – NO INVERTED REGION! (at least for reasonable driving forces)



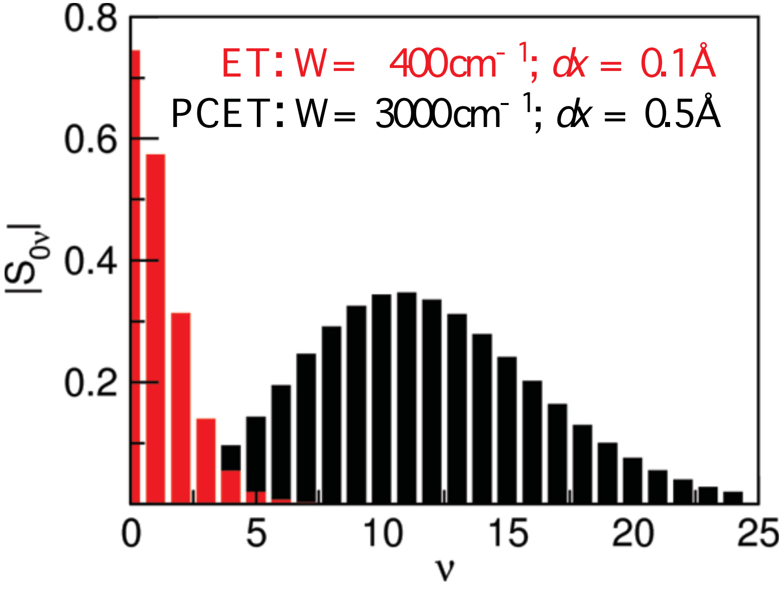


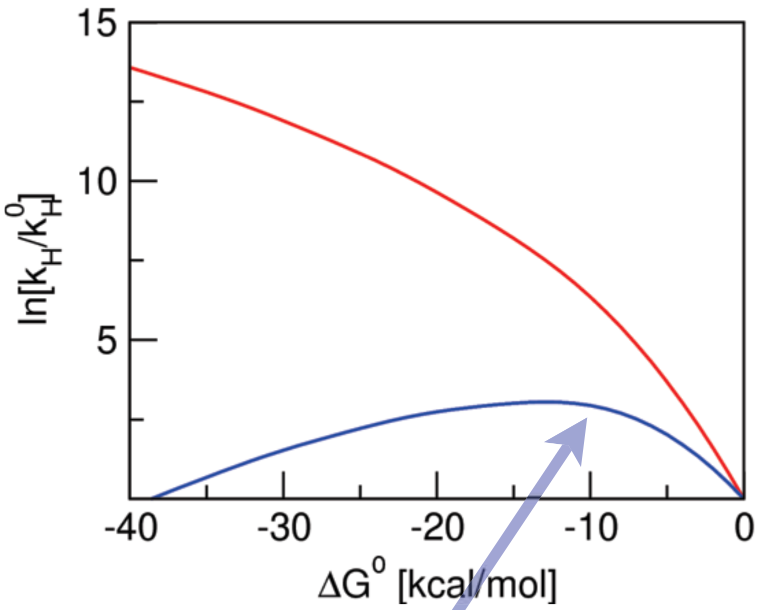
[Edwards, Soudackov, SHS, JPC A 2009; JPC B 113, 14545 (2009)]

Free energy relationship for PCET

What is a key difference between ET (with reorganizing intramolecular mode) and PCET with proton transferring (“reorganizing”)?

Overlap integrals





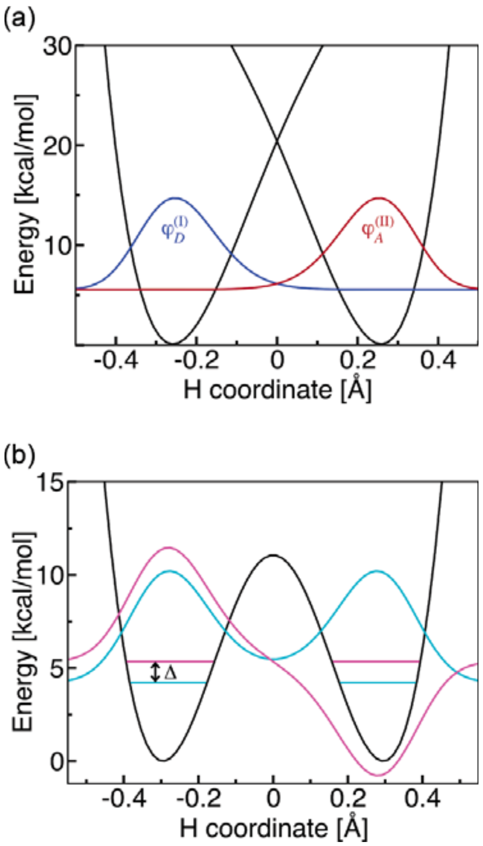
However, inverted region in PCET is possible (blue curve) if proton donor-acceptor distance increases for more negative driving forces

[Edwards, Soudackov, SHS, JPC A 2009; JPC B 113, 14545 (2009)]

Electron-Proton adiabaticity: HAT vs.

Classification based on the vibronic coupling calculation?

Georgievskii, Stuchebrukhov (2000): $V_{DA} = \kappa V_{DA}^{(ad)}$, $\kappa = \sqrt{2\pi p}\,\frac{\exp[p\ln p - p]}{\Gamma(p+1)}$



Electronically non-adiabatic PT:

$$p = \frac{\tau_p}{\tau_{el}} \ll 1: \quad V_{DA} \to V_{DA}^{(na)} = V^{el}\left\langle \varphi_D^{(I)} \middle| \varphi_D^{(II)} \right\rangle$$

[p – adiabaticity parameter (semiclassical)]

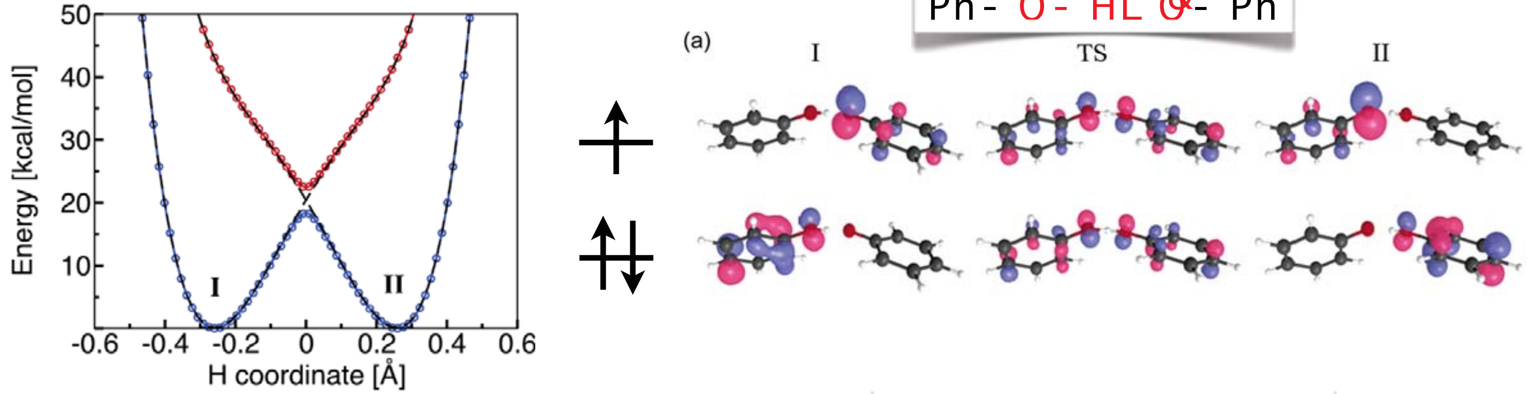
Electronically adiabatic PT:

$$p = \frac{\tau_p}{\tau_{el}} \gg 1: \quad V_{DA} \to V_{DA}^{(ad)} = \frac{\Delta}{2}$$

[Skone, Soudackov, SHS, JACS 2006]

Electron–Proton adiabaticity: HAT vs.

Ph- O- HL O&- Ph



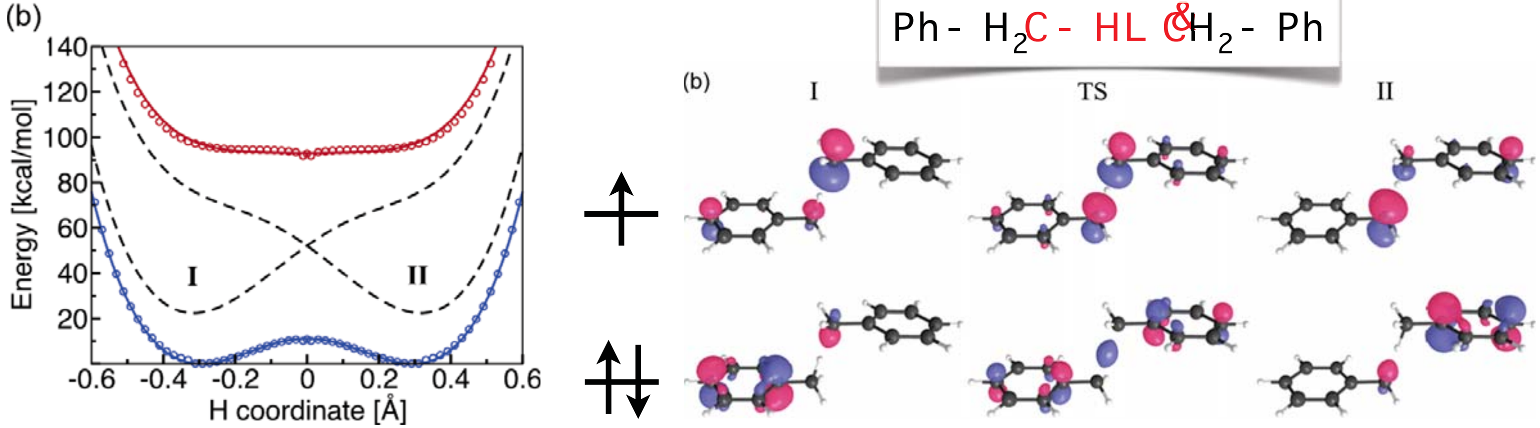
PCET

t_p = 0.098fs

t_{el} = 7.60fs

p = 0.0130

Ph- H$_2$C- HL C&H$_2$- Ph



HAT

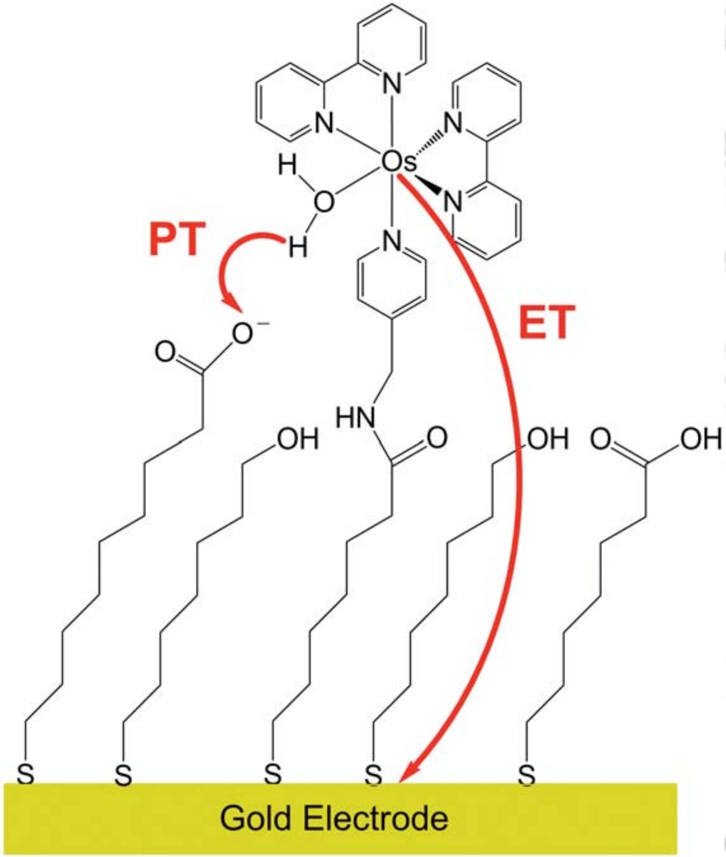
t_p = 1.28fs

t_{el} = 0.37fs

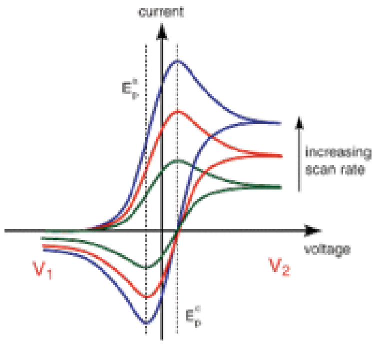
p = 3.45

[Skone, Soudackov, SHS, JACS 2006]

Electrochemical PCET



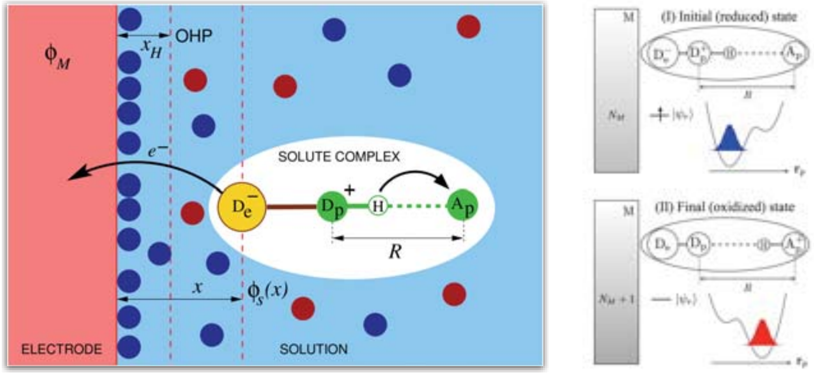
Electrochemical PCET



- Advantages of electrochemical PCET
  - reaction can be easily controlled through the electrode potential
  - measurements are performed using nondestructive techniques (e. g. cyclic voltammetry)
  - measurable observables (current density) are directly related to the elementary act (no need to isolate the ET/PCET step)
  - reactive species can be chemically attached to the electrode surface (e. g. via SAM) – fixed ET distance and no double layer effects
  - realatively easy to measure kinetic isotope effects (KIE) – reliable probe for “PC” part in “PCET”

Electrochemical PCET: Concerted Model

$$\mathrm{SC} + \mathrm{M} \rightleftharpoons \mathrm{SC}^{+} + \mathrm{M}\,[e^{-}(\varepsilon_m)]$$



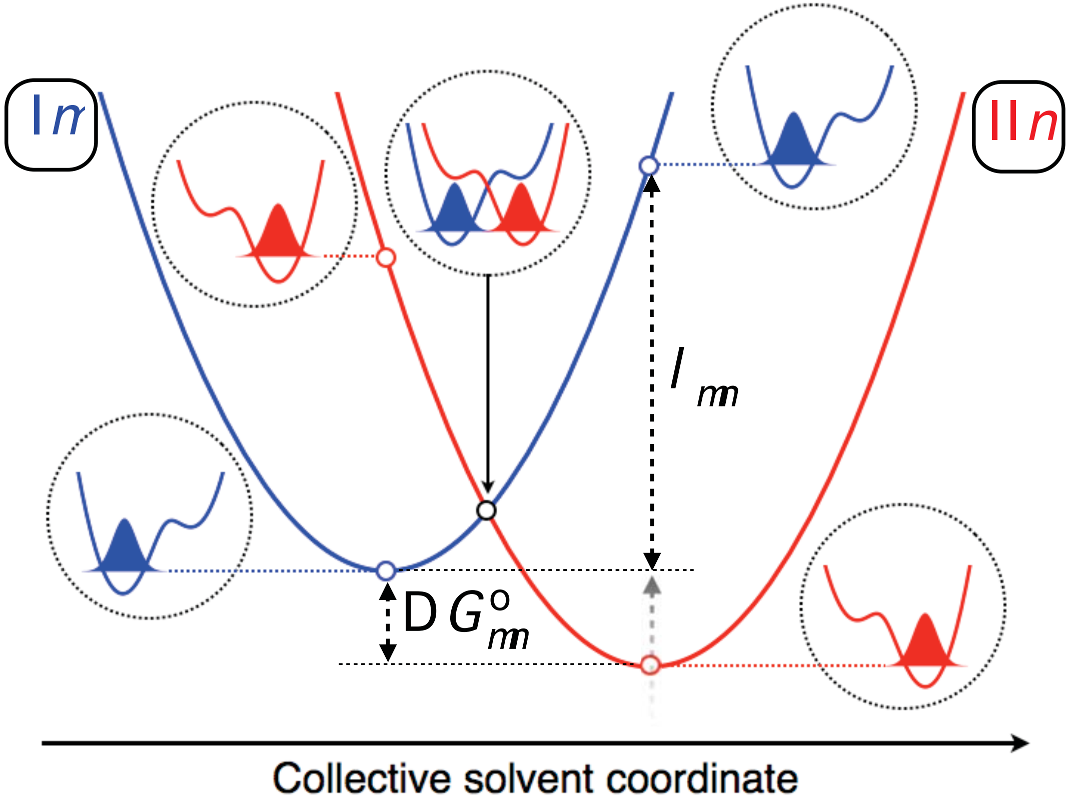
- Solute complex with preformed hydrogen bonded PT interface (fast equilibrium with large K_{assoc})
- Proton acceptor (A_p) can be part of the redox species or a (buffer) molecule in solution
- Quasi-free electron model for the metal electrode

$$f(\epsilon_m) = \left[1 + e^{\beta \epsilon_m}\right]^{-1}$$

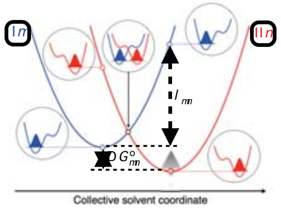
- Significantly different asymmetric proton potentials for reduced and oxidized forms of the solute complex

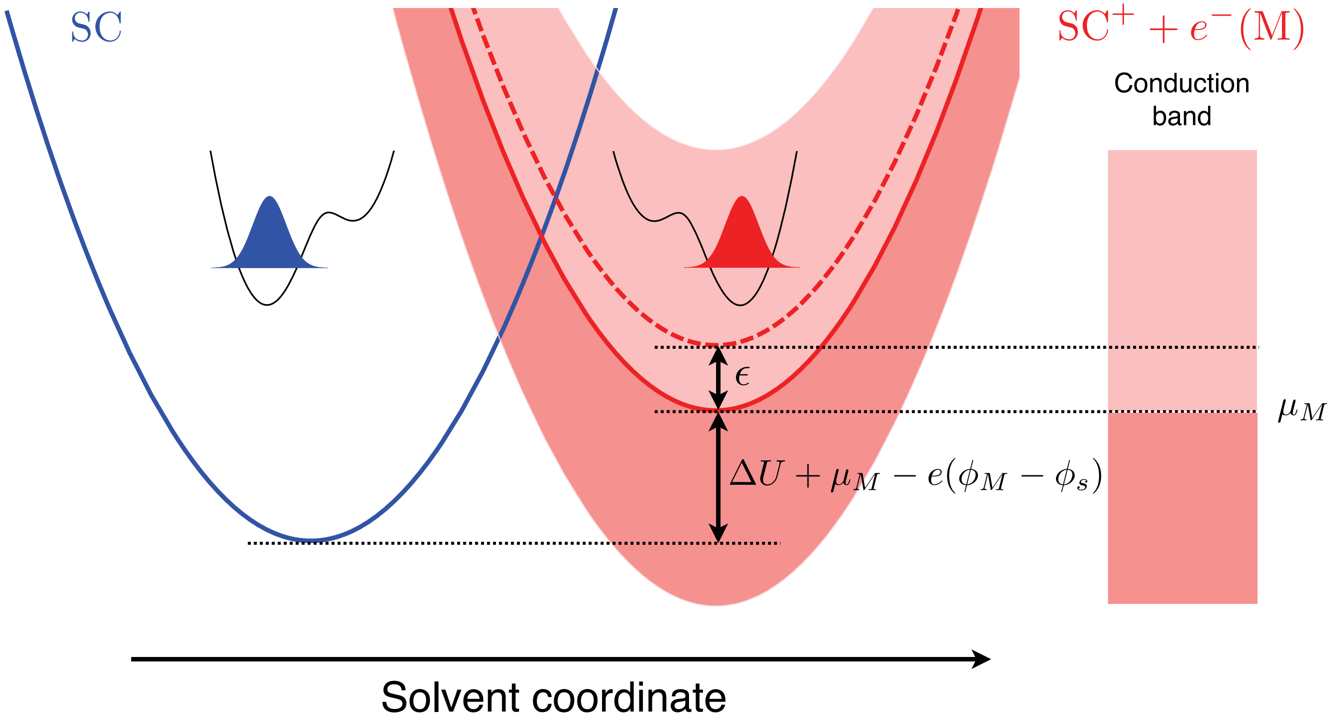
[Venkataraman, Soudackov, Hammes-Schiffer: J. Phys. Chem. C 2008]

Electrochemical PCET: nonadiabatic

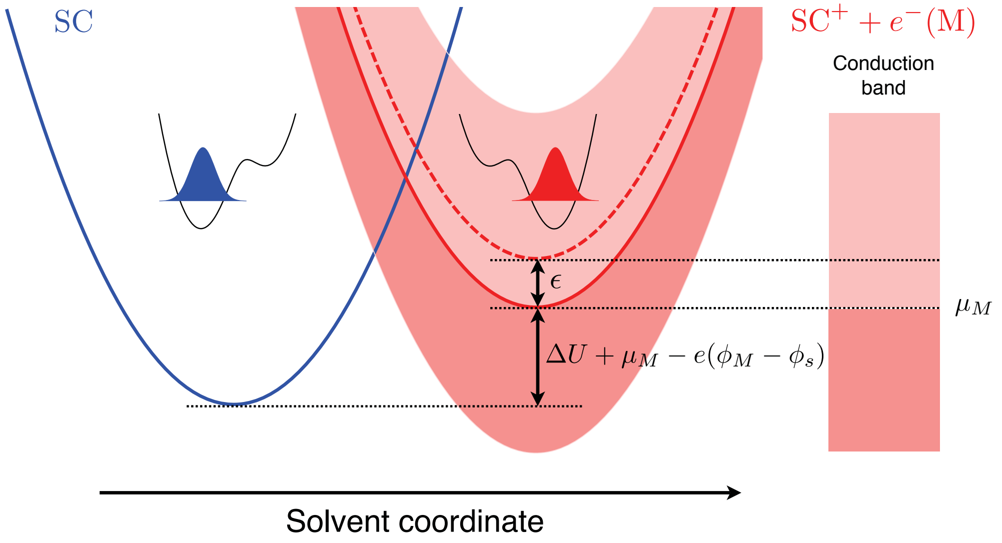


Electrochemical PCET: nonadiabatic





Electrochemical PCET: nonadiabatic



Vibronic couplings at equilibrium donor-acceptor distance R₀ for the reduced complex:

$$V^0_{\mu\nu}(x,\varepsilon) \approx V^{el}(x,\varepsilon)S_{\mu\nu}(R_0)$$

Free energy differences:

$$\Delta G_{\mu\nu}(x,\varepsilon) = \Delta U_{\mu\nu} + k_B T \ln\frac{Q^{II}}{Q^{I}} + \varepsilon - e[\eta - \phi_s(x)]$$

overpotential

electronic level in the metal

Electrochemical PCET: nonadiabatic

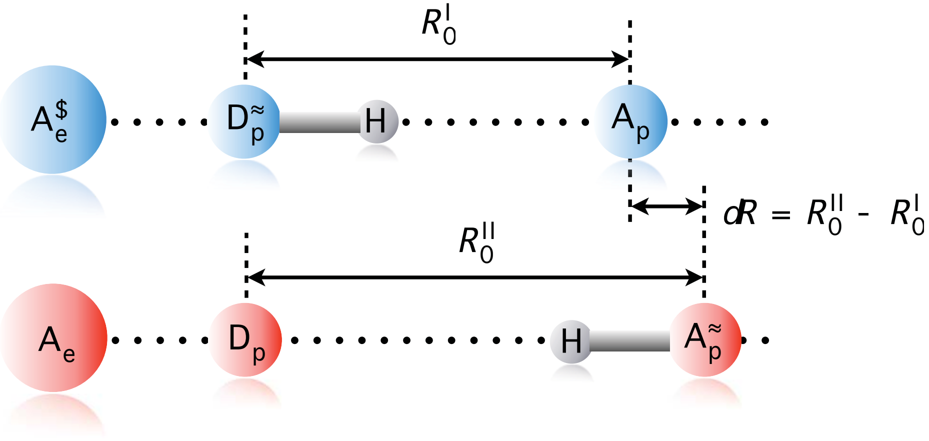
Oxidation (anodic) and reduction (cathodic) transition probabilities:

$$W_{\mathrm{SC}\to\mathrm{M}}(x,\varepsilon)=\frac{1}{\hbar}\sum_{\mu,\nu}P_\mu\left|V^0_{\mu\nu}(x,\varepsilon)\right|^2\exp\left[\frac{2k_BT\alpha^2_{\mu\nu}}{M\Omega^2}\right]\sqrt{\frac{\pi}{k_BT\Lambda_{\mu\nu}}}\times\exp\left[-\frac{\left(\Delta G_{\mu\nu}(x,\varepsilon)+\Lambda_{\mu\nu}+2k_BT\alpha_{\mu\nu}\delta R\right)^2}{4k_BT\Lambda_{\mu\nu}}\right]$$

$$W_{\mathrm{M}\to\mathrm{SC}^+}(x,\varepsilon)=\frac{1}{\hbar}\sum_{\mu,\nu}P_\mu\left|V^0_{\mu\nu}(x,\varepsilon)\right|^2\exp\left[\frac{2k_BT\alpha^2_{\mu\nu}}{M\Omega^2}-2\alpha_{\mu\nu}\delta R\right]\sqrt{\frac{\pi}{k_BT\Lambda_{\mu\nu}}}\times\exp\left[-\frac{\left(-\Delta G_{\mu\nu}(x,\varepsilon)+\Lambda_{\mu\nu}-2k_BT\alpha_{\mu\nu}\delta R\right)^2}{4k_BT\Lambda_{\mu\nu}}\right]$$

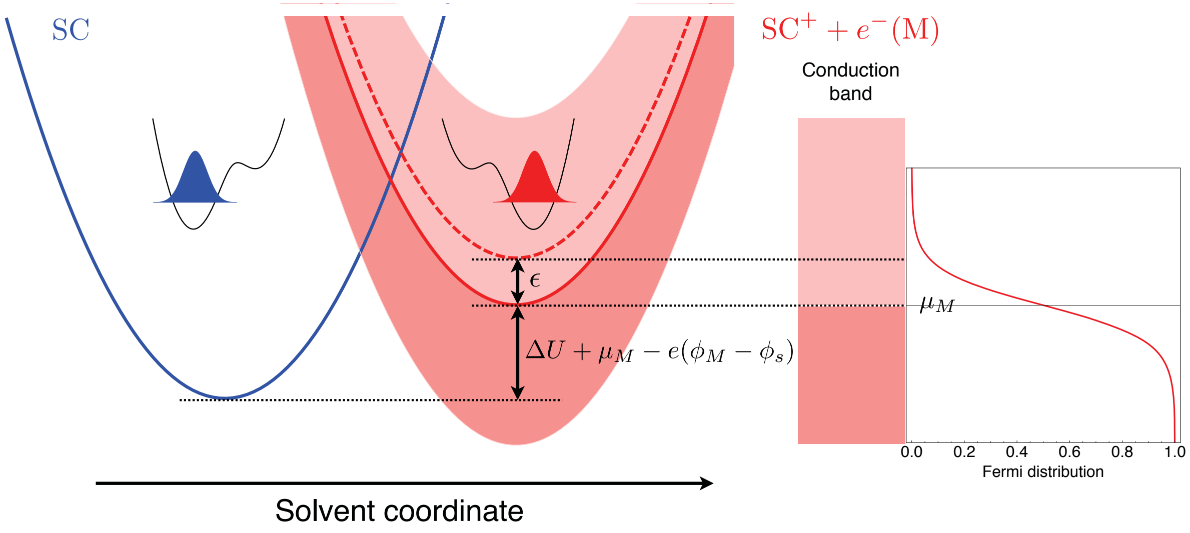
Reduced solute complex:

Oxidized solute complex:



$\delta R = R_0^{\mathrm{II}} - R_0^{\mathrm{I}}$

Electrochemical PCET: rate constants



x–dependent anodic and cathodic first order rate constants:

$$k_a(x) = \int d\epsilon [1 - f(\epsilon)]\rho(\epsilon) W_{SC\to M}(x,\epsilon)$$

$$k_c(x) = \int d\epsilon \, f(\epsilon)\rho(\epsilon) W_{M\to SC^+}(x,\epsilon)$$

In the vicinity of the Fermi level: $\rho(\epsilon)\left|V^{el}(x,\epsilon)\right|^2 \approx \rho(\epsilon_F)\left|V^{el}(x,\epsilon_F)\right|^2$

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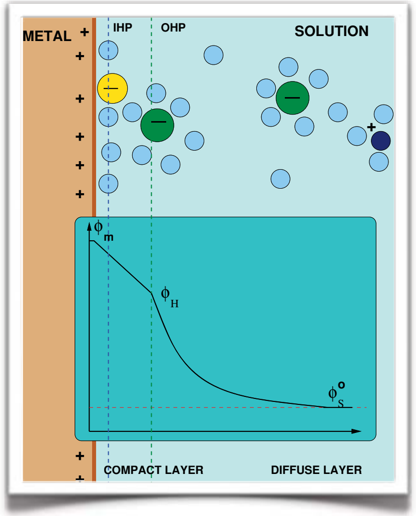
Electrochemical PCET: current densities

- Exponential dependence of the coupling on the distance x to the electrode surface (for nonadiabatic ET $\beta' \approx 1$ Å^{-1})
- Gouy-Chapman-Stern model: low electrolyte concentrations, large Debye length ($\beta' \gg \kappa$) – current is dominated by PCET at the outer

ψ – potential at outer Helmhotz plane



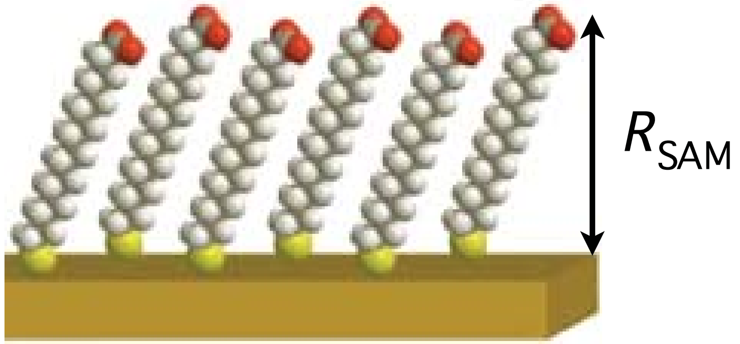
$$j_a(\eta) = F\int_{x_H}^{\infty} dx\, C_{SC}(x) k_a(x,\eta) \approx F C_{SC}^{\infty} \frac{k_a(x_H,\eta)}{\beta'} e^{-z\beta e\psi}$$

$$j_c(\eta) = F\int_{x_H}^{\infty} dx\, C_{SC^+}(x) k_c(x,\eta) \approx F C_{SC^+}^{\infty} \frac{k_c(x_H,\eta)}{\beta'} e^{-(z+1)\beta e\psi}$$

[Venkataraman, Soudackov, Hammes-Schiffer: J. Phys. Chem. C 2008]

Electrochemical PCET: current densities

- For redox species chemically attached to SAM on the electrode



$$j_{\mathrm{a}}(h) = eC_{\mathrm{SC}}^{\mathrm{cov}}(R_{\mathrm{SAM}})\, k_{\mathrm{a}}(R_{\mathrm{SAM}}, h)$$

$$j_{\mathrm{c}}(h) = eC_{\mathrm{SC^+}}^{\mathrm{cov}}(R_{\mathrm{SAM}})\, k_{\mathrm{c}}(R_{\mathrm{SAM}}, h)$$

Electrochemical PCET: transfer

- defined via logarithmic derivative of the cathodic current density

$$a_{\mathrm{PCET}}(h) = - \frac{1}{k_{\mathrm{B}}T} \frac{d \ln j_{\mathrm{c}}(h)}{d(eh)}$$

- approximate expression
  - (ignore the effects of the excited vibronic states)
  - (assume that electron transfers only to/from the Fermi level)

$$a_{\mathrm{PCET}}(h) \ ^{\mathrm{a}} \ \frac{1}{2} - \frac{k_{\mathrm{B}}T\, a_{00} dR}{\mathrm{L}} + \frac{eh}{2\mathrm{L}}$$

Electrochemical PCET: transfer

- defined via logarithmic derivative of the cathodic current density

$$a_{\mathrm{PCET}}(h) = -\frac{1}{k_B T}\frac{d \ln j_c(h)}{d(eh)}$$

- approximate expression
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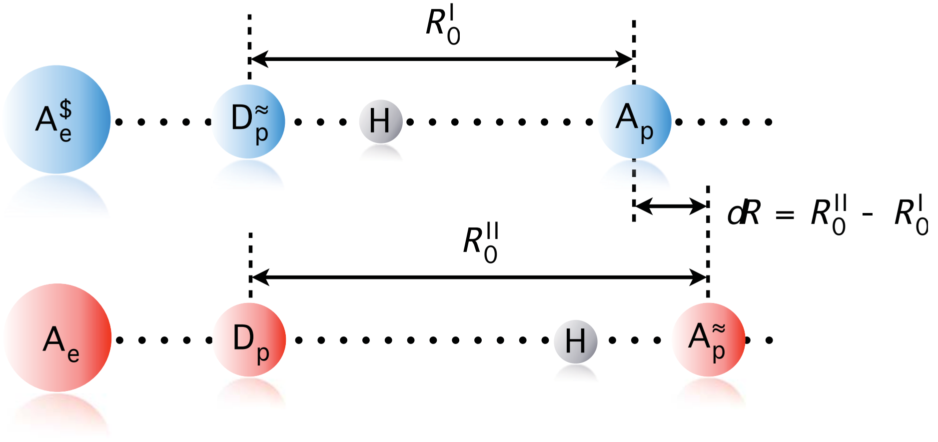
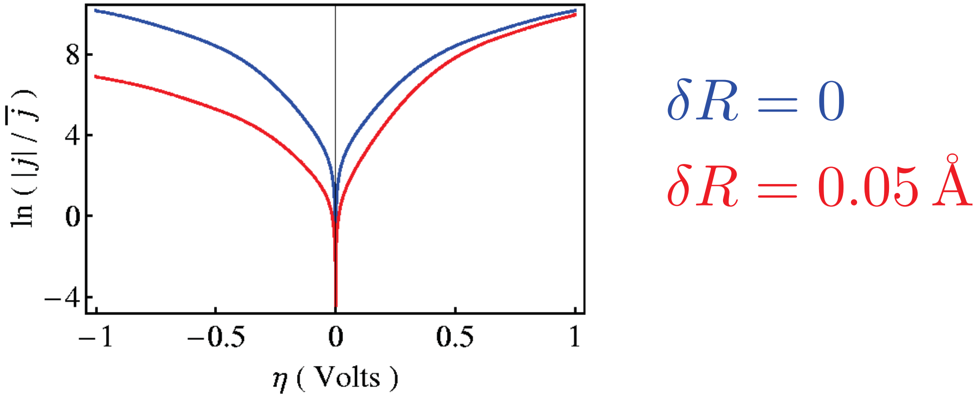
$$a_{\mathrm{PCET}}(h) \text{ a } \frac{1}{2} - \frac{k_B T a_{00} dR}{L} + \frac{eh}{2L}$$



- deviation from standard value of 1/2: due to different equilibrium proton donor-acceptor distances in reduced and oxidized solute

Electrochemical PCET: main features

- Observable kinetic isotope effects (KIE) (up to ~4 reported)
- Different “effective” temperature dependent activation energies for cathodic and anodic processes (terms $\pm 2k_{\mathrm{B}}T\alpha_{\mu\nu}\delta R$ on the order of a few kcal/mol)



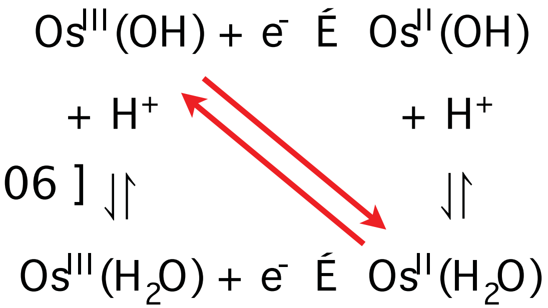
- transfer coefficient deviates from 0.5:

$$\alpha_{\mathrm{PCET}}(\eta) \approx \frac{1}{2} - \frac{\alpha_{00}\delta R}{\beta\Lambda_{00}} + \frac{e\eta}{2\Lambda_{00}}$$

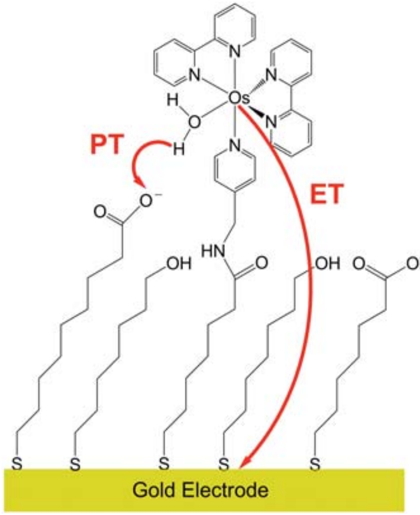
Electrochemical PCET: application

$[\mathrm{Os^{II}(bpy)_2(4\text{-}aminomethylpyridine)(H_2O)}]^{2+}$ attached to a mixed self-assembled monolayer on a gold electrode

Experimental data [Madhiri, Finklea: Langmuir 2006]

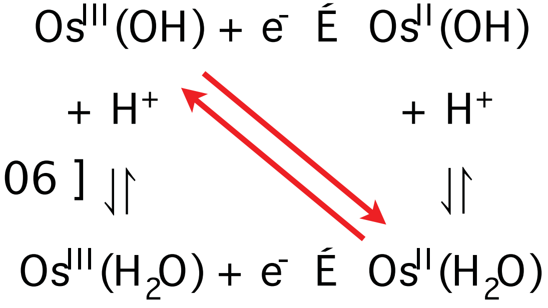


$$\begin{tikzcd}
\mathrm{Os^{III}(OH)} + e^- \arrow[r, phantom, "\rightleftharpoons"] & \mathrm{Os^{II}(OH)} \\
+\ \mathrm{H^+} \arrow[d, shift left] & +\ \mathrm{H^+} \arrow[d, shift left] \\
\mathrm{Os^{III}(H_2O)} + e^- \arrow[u, shift left] \arrow[r, phantom, "\rightleftharpoons"] & \mathrm{Os^{II}(H_2O)} \arrow[u, shift left] \arrow[uul, shift left] \arrow[uul, leftarrow, shift right]
\end{tikzcd}$$



Electrochemical PCET: application

[$Os^{II}(bpy)_2$(4-aminomethylpyridine)$(H_2O)]^{2+}$ attached to a mixed self-assembled monolayer on a gold electrode



$Os^{III}(OH) + e^-$ É $Os^{II}(OH)$

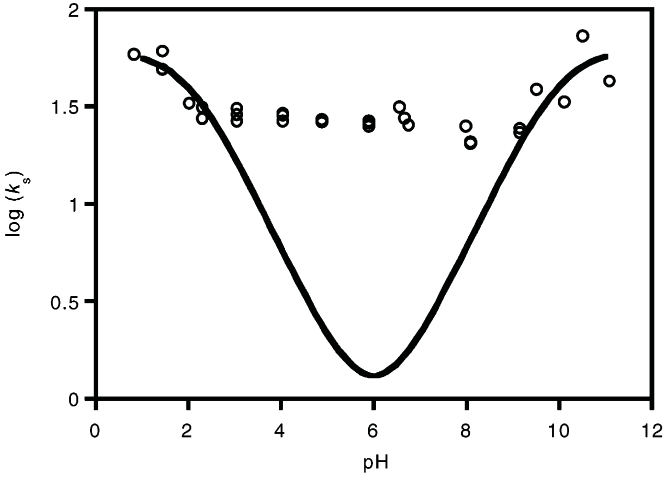
+ H^+ + H^+

⇃↾ ⇃↾

$Os^{III}(H_2O) + e^-$ É $Os^{II}(H_2O)$

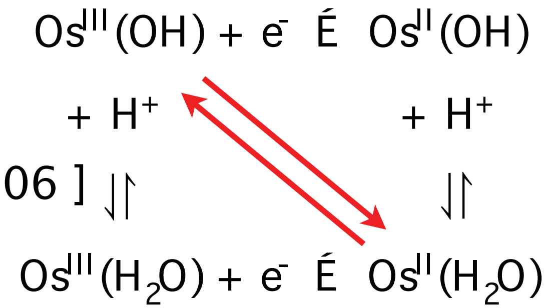
Experimental data [Madhiri, Finklea: Langmuir 2006]

- concerted PCET mechanism (data incompatible with the stepwise model)



Electrochemical PCET: application

$[Os^{II}(bpy)_2(4\text{-aminomethylpyridine})(H_2O)]^{2+}$ attached to a mixed self-assembled monolayer on a gold electrode

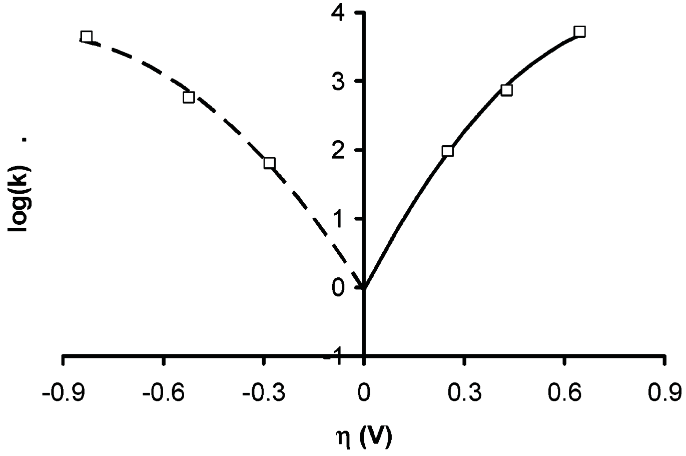

$Os^{III}(OH) + e^-$ É $Os^{II}(OH)$

$+ H^+$ $+ H^+$

$Os^{III}(H_2O) + e^-$ É $Os^{II}(H_2O)$

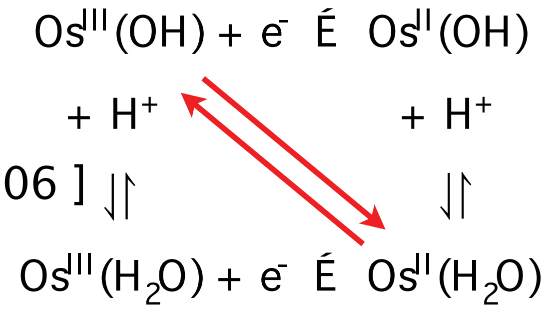
Experimental data [Madhiri, Finklea: Langmuir 2006]

- concerted PCET mechanism (data incompatible with the stepwise model)
- Kinetic isotope effect KIE ≈ 2 at pH ~ 4 ⇒ proton acceptor: COO^- group (SAM) with $pK_a \approx 5$
- asymmetric Tafel plot with higher anodic currents (suggested two different reorganization energies for cathodic and anodic processes)



Electrochemical PCET: application

$[Os^{II}(bpy)_2(4\text{-aminomethylpyridine})(H_2O)]^{2+}$ attached to a mixed self-assembled monolayer on a gold electrode



$Os^{III}(OH) + e^- \rightleftharpoons Os^{II}(OH)$

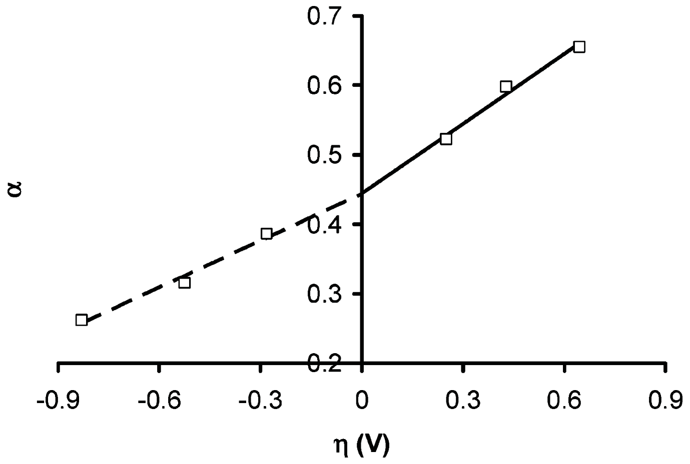
$+ H^+$ $\qquad$ $+ H^+$

$\downarrow\uparrow$ $\qquad$ $\downarrow\uparrow$

$Os^{III}(H_2O) + e^- \rightleftharpoons Os^{II}(H_2O)$

Experimental data [Madhiri, Finklea: Langmuir 2006]

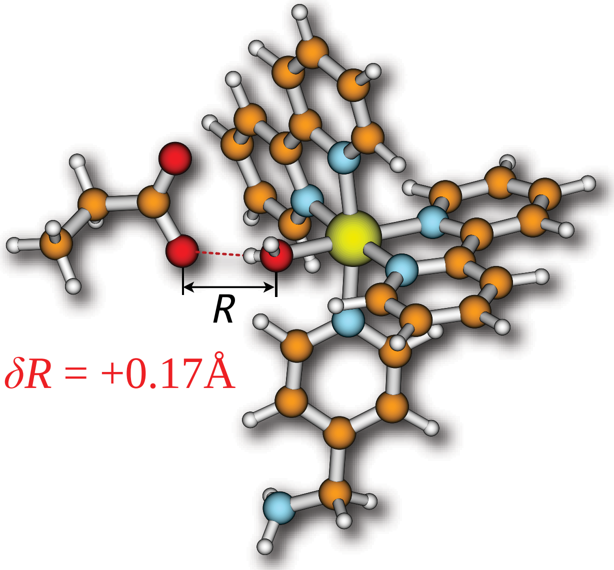
- concerted PCET mechanism (data incompatible with the stepwise model)
- Kinetic isotope effect KIE ≈ 2 at pH ~ 4 ⇒ proton acceptor: COO^- group (SAM) with $pK_a \approx 5$
- asymmetric Tafel plot with higher anodic currents (suggested two different reorganization energies for cathodic and anodic processes)
- Observed strong potential dependence of the transfer coefficient (0.2–0.8) (non–linear free energy relationship): $\alpha(0) = 0.46 \pm$



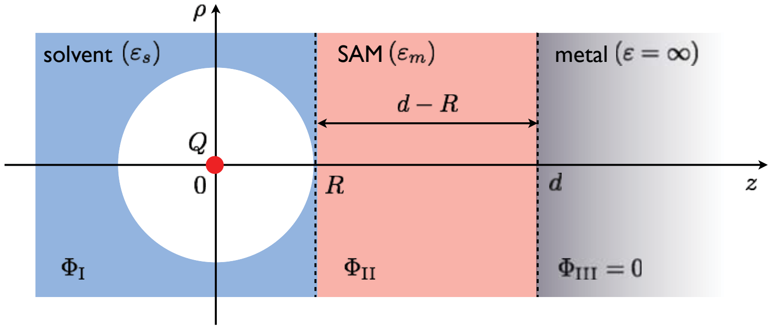
Electrochemical PCET: application

Theoretical modeling: input parameters

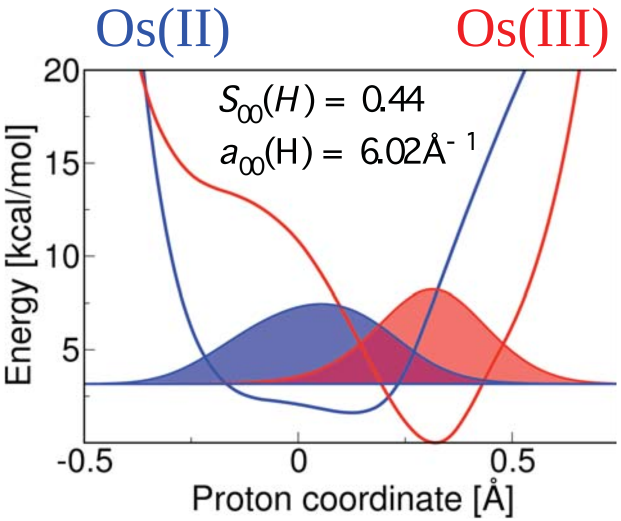
- DFT (B3LYP) calculations of optimized geometries and proton profiles for reduced and oxidized Os complexes: $\delta R_{\text{O-O}} = +0.17\text{Å}$ (reduced: 2.49Å and oxidized: 2.66Å)
- proton vibrational wavefunctions generated using Fourier Grid Hamiltonian method



$\delta R = +0.17\text{Å}$



[Liu, Newton, 1994]



[Ludlow, Soudackov, Hammes-Schiffer: JACS 2010]

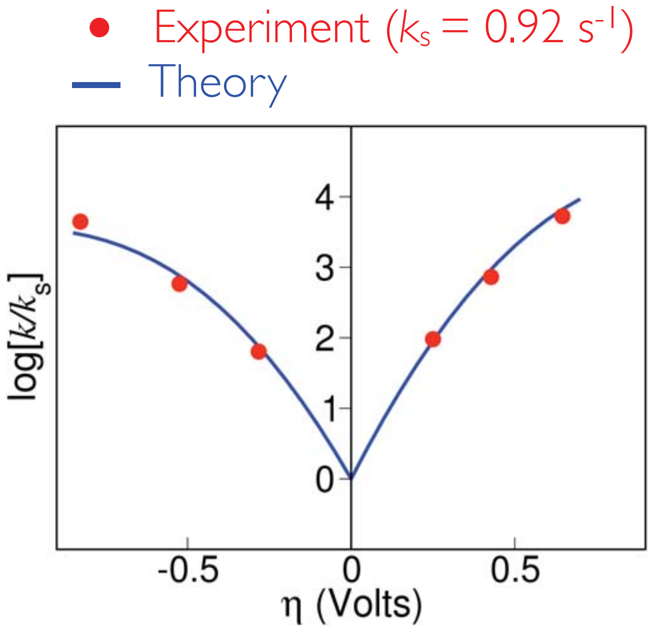
Electrochemical PCET: application

Theoretical modeling: no fitting to experimental data!

- reproduced asymmetric Tafel plot
- calculated transfer coefficient $\alpha(0) = 0.47$ (c.f. experimental value of 0.46 ± 0.02)

$$a_{PCET}(0) \; a \; \frac{1}{2} - \frac{k_B T a_{00} dR}{L}$$

- calculated KIE for the standard rate constant: KIE ~ 2.0 (c.f. experim. value of KIE ~ 2)
- ruled out H_2O as proton acceptor: $\delta R < 0$



[Ludlow, Soudackov, Hammes-Schiffer: JACS 2010]

Conclusions

- Simple four-state model (1a-1b-2a-2b) describes essential physics of PCET processes
  - can also describe all possible fundamental mechanisms (next talk)
- Majority of concerted PCET reactions are vibronically non-adiabatic
- Electron-proton adiabaticity parameter can be used to distinguish HAT (electronically adiabatic PT) and PCET (electronically non-adiabatic PT)
- Proton donor-acceptor vibrational motion has important effects on the rates and isotope effects
- Model can explain (and predict?) trends in rates and isotope effects
  - PCET in polar solvents
  - electrochemical PCET

- Photoinduced PCET dynamics!

Acknowledgements

- **Financial support**
  - NSF
  - AFOSR
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  - NSF Center for Chemical Innovation (

Thank you!