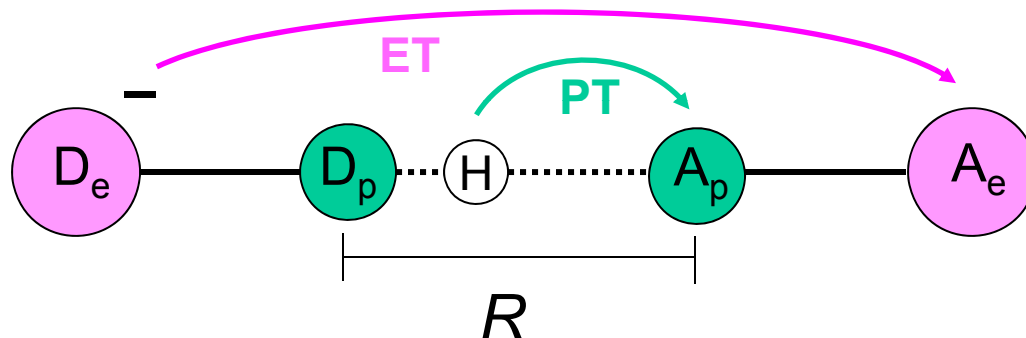


Theory of Proton-Coupled Electron Transfer

Sharon Hammes-Schiffer
Pennsylvania State University

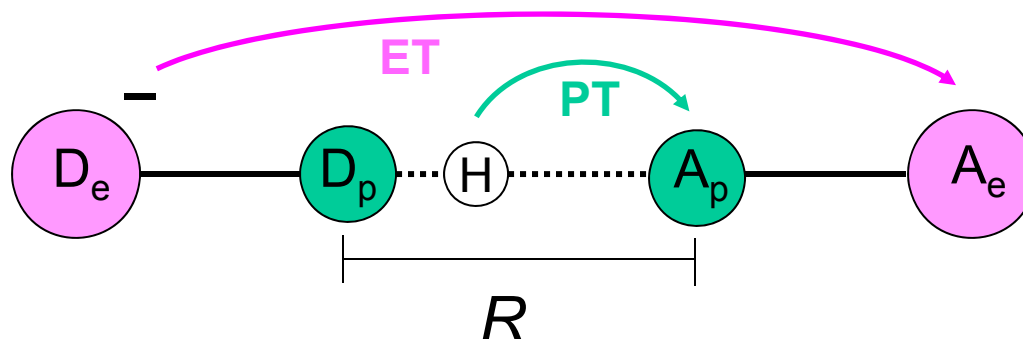


Note: Much of this information, along with more details, additional rate constant expressions, and full references to the original papers, is available in the following JPC Feature Article:

Hammes-Schiffer and Soudackov, JPC B **112**, 14108 (2008)

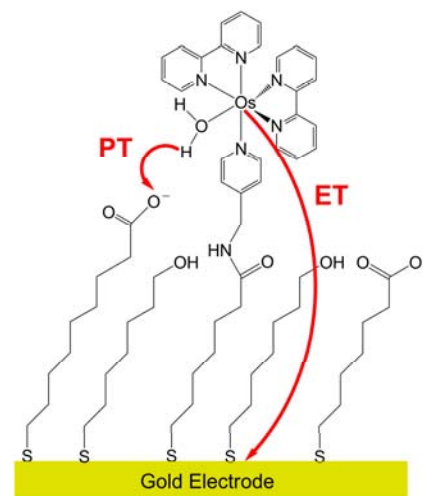
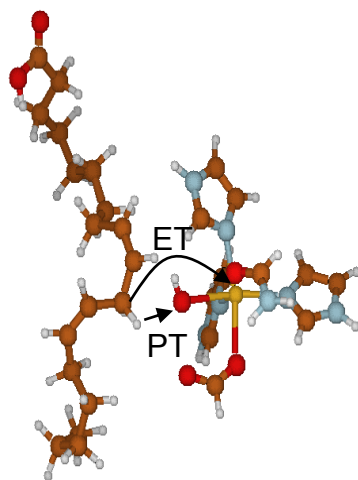
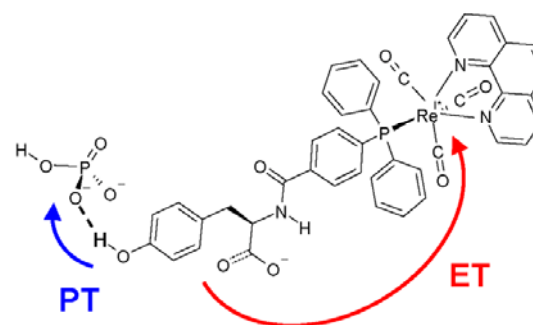
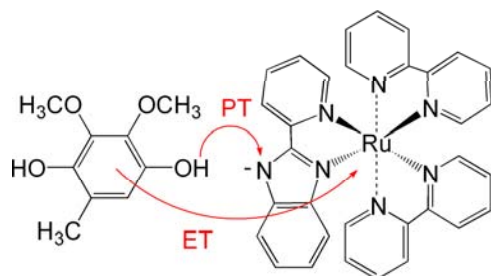
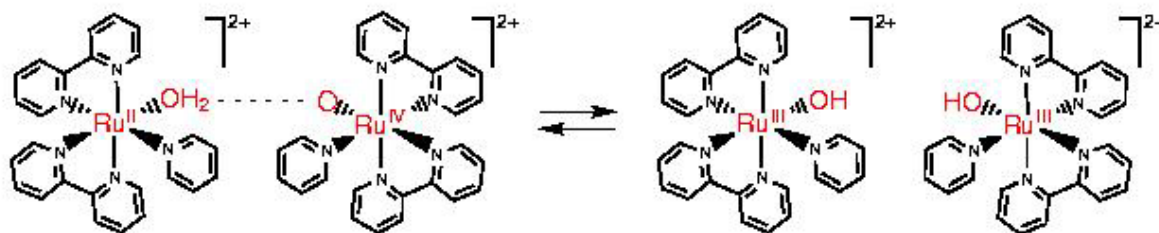
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General Definition of PCET



- Electron and proton transfer reactions are coupled
- Electron and proton donors/acceptors can be the same or different
- Electron and proton can transfer in the same direction or in different directions
- Concerted vs. sequential PCET discussed below
- Concerted PCET is also denoted CPET and EPT
- Hydrogen atom transfer (HAT) is a subset of PCET
- Distinction between PCET and HAT discussed below

Examples of Concerted PCET



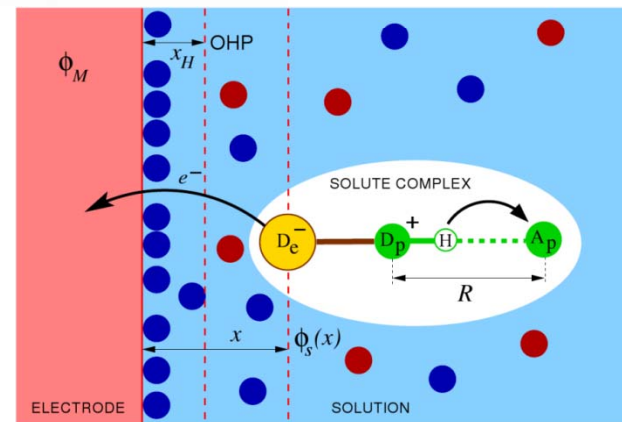
Importance of PCET

- Biological processes
 - photosynthesis
 - respiration
 - enzyme reactions
 - DNA



Cytochrome c oxidase
 $4e^- + 4H^+ + O_2 \rightarrow 2(H_2O)$

- Electrochemical processes
 - fuel cells
 - solar cells
 - energy devices



Theoretical Challenges of PCET

- Wide range of timescales
 - Solute electrons
 - Transferring proton(s)
 - Solute modes
 - Solvent electronic/nuclear polarization
- Quantum behavior of electrons and protons
 - Hydrogen tunneling
 - Excited electronic/vibrational states
 - Adiabatic and nonadiabatic behavior
- Complex coupling among electrons, protons, solvent

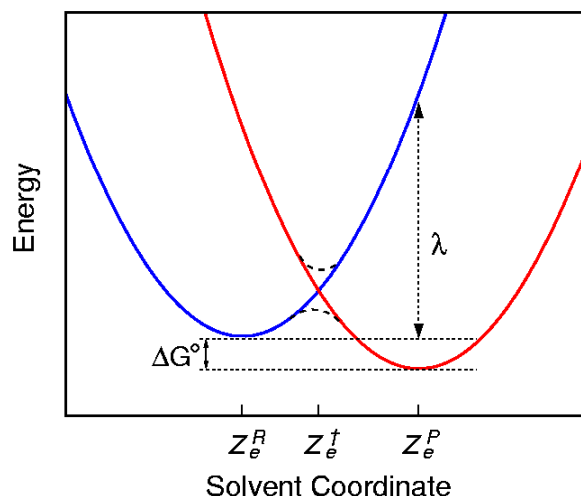
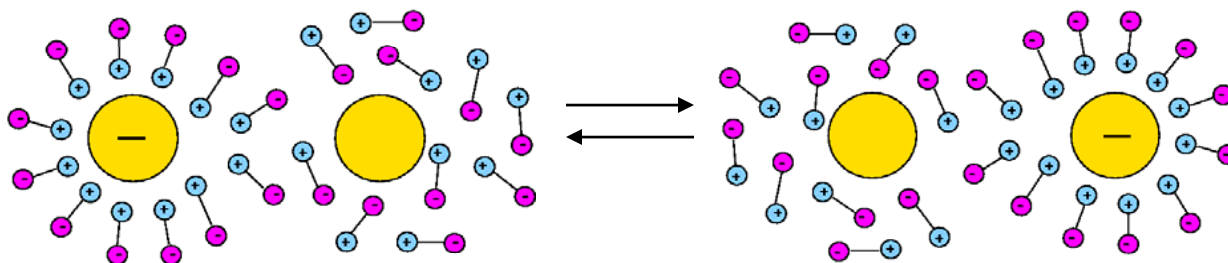
Single Electron Transfer

Diabatic states:



Solvent coordinate

$$z_e = \int d\mathbf{r}(\rho_2 - \rho_1)\Phi_{in}(\mathbf{r})$$



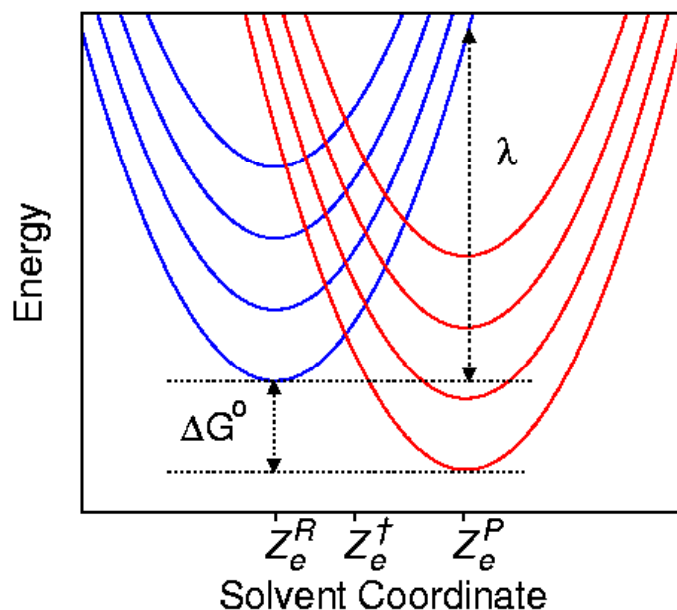
Marcus theory

Nonadiabatic ET rate: $k = \frac{2\pi}{\hbar} V_{12}^2 (4\pi\lambda k_B T)^{-1/2} \exp\left[-\Delta G^\ddagger / (k_B T)\right]$

$$\Delta G^\ddagger = (\Delta G^0 + \lambda)^2 / (4\lambda)$$

V_{12} : coupling between diabatic states

Inner-Sphere Solute Modes



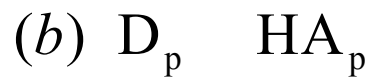
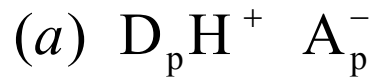
$$k = \frac{2\pi}{\hbar} V_{12}^2 (4\pi\lambda k_B T)^{-1/2} \sum_{\mu} P_{\mu}^I \sum_{\nu} \left| \langle \varphi_{\mu}^{(1)} | \varphi_{\nu}^{(2)} \rangle \right|^2 \exp \left[-\Delta G_{1\mu, 2\nu}^{\ddagger} / (k_B T) \right]$$

vibrational wavefunctions $\varphi_{\mu}^{(1)}$, $\varphi_{\nu}^{(2)}$

Assumes solute mode is not coupled to solvent →
 Not directly applicable to PCET because proton strongly coupled to solvent

Single Proton Transfer

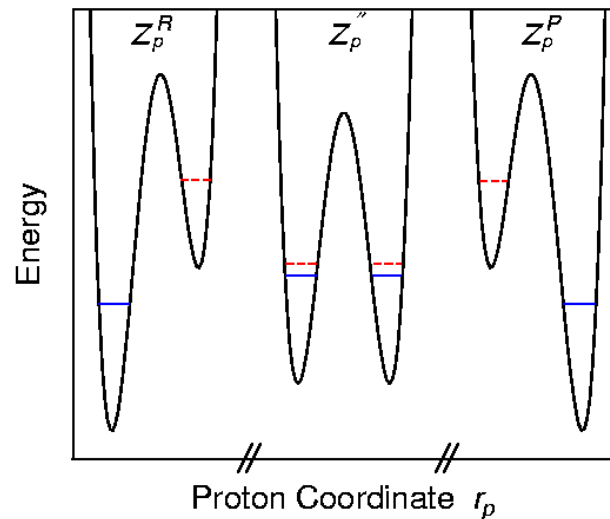
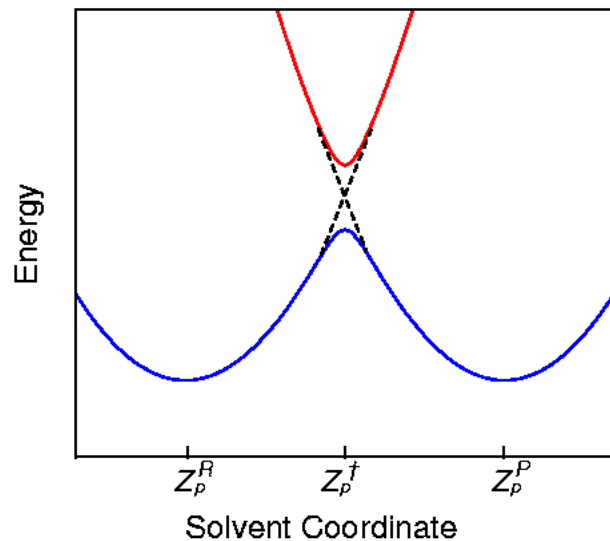
Diabatic states:



Solvent coordinate

$$z_p = \int d\mathbf{r} (\rho_b - \rho_a) \Phi_{in}(\mathbf{r})$$

Proton coordinate: r_p (QM)



PT typically electronically adiabatic (occurs on ground electronic state) but can be vibrationally adiabatic or nonadiabatic

Proton-Coupled Electron Transfer

Soudackov and Hammes-Schiffer, JCP 111, 4672 (1999)

- Four diabatic states:
 - (1a) $D_e^- \text{---} {}^+ D_p H \cdots A_p \text{---} A_e$
 - (1b) $D_e^- \text{---} D_p \cdots H A_p^+ \text{---} A_e$
 - (2a) $D_e \text{---} {}^+ D_p H \cdots A_p \text{---} A_e^-$
 - (2b) $D_e \text{---} D_p \cdots H A_p^+ \text{---} A_e^-$

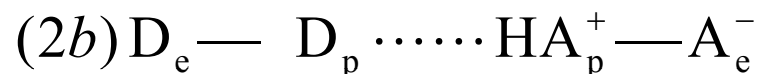
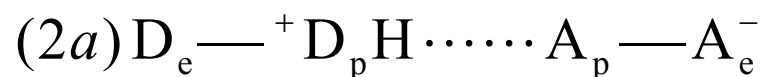
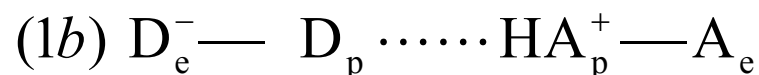
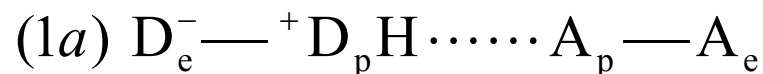
- Free energy surfaces depend on 2 collective solvent coordinates z_p, z_e

$$\text{PT } (1a) \rightarrow (1b): \quad z_p = \int d\mathbf{r} (\rho_{1b} - \rho_{1a}) \Phi_{\text{in}}(\mathbf{r})$$

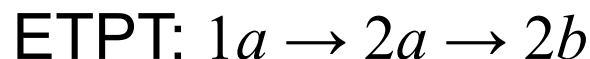
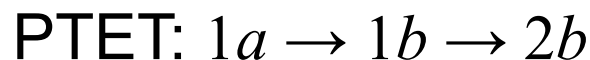
$$\text{ET } (1a) \rightarrow (2a): \quad z_e = \int d\mathbf{r} (\rho_{2a} - \rho_{1a}) \Phi_{\text{in}}(\mathbf{r})$$

- Extend to N charge transfer reactions with 2^N states and N collective solvent coordinates

Sequential vs. Concerted PCET



- **Sequential:** involves stable intermediate from PT or ET



- **Concerted:** does not involve a stable intermediate



- Mechanism is determined by relative energies of diabatic states and couplings between them
- $1b$ and $2a$ much higher in energy \rightarrow concerted EPT

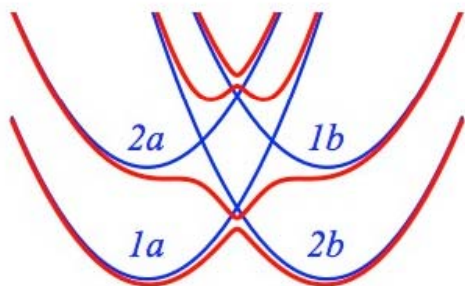
Reactant and Product Diabatic States

Remaining slides focus on “concerted” PCET:
describe in terms of **Reactant** → **Product**

- Reactant diabatic state (I)
 - electron localized on donor D_e
 - mixture of $1a$ and $1b$ states
- Product diabatic state (II)
 - electron localized on acceptor A_e
 - mixture of $2a$ and $2b$ states

Typically large coupling between a and b PT states and
smaller coupling between 1 and 2 ET states

Diabatic vs. Adiabatic Electronic States

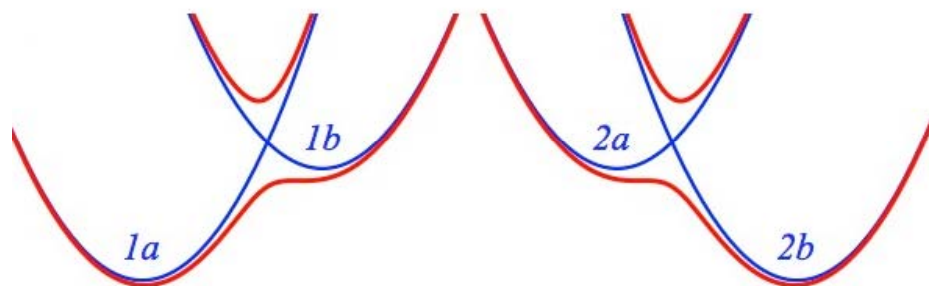


4 diabatic states: $1a, 1b, 2a, 2b$

4 adiabatic states:

Diagonalize 4×4 Hamiltonian matrix in basis of 4 diabatic states

Typically highest 2 states can be neglected

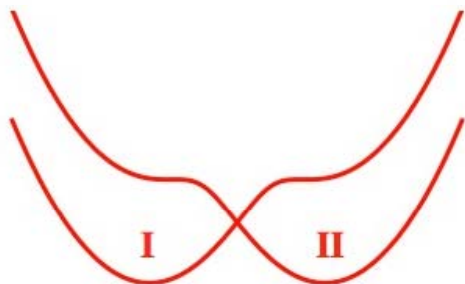


2 pairs of diabatic states: $1a/1b, 2a/2b$

2 pairs of adiabatic states:

Block diagonalize $1a/1b, 2a/2b$ blocks

Typically excited states much higher in energy and can be neglected



2 ground adiabatic states from block diagonalization above:

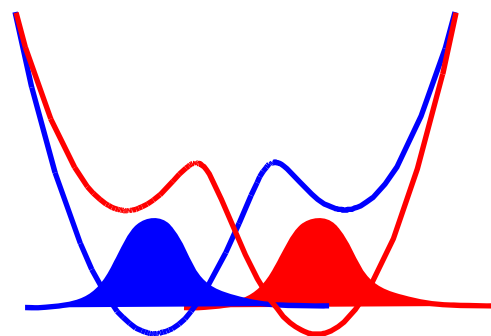
Reactant (I) and Product (II) diabatic states for overall PCET reaction

Electron-Proton Vibronic States

H treated quantum mechanically

Calculate proton vibrational states for electronic states I and II

- electronic states: $\Psi_I(\mathbf{r}_e, \mathbf{r}_p)$, $\Psi_{II}(\mathbf{r}_e, \mathbf{r}_p)$
- proton vibrational states: $\varphi_{I\mu}(\mathbf{r}_p)$, $\varphi_{II\nu}(\mathbf{r}_p)$



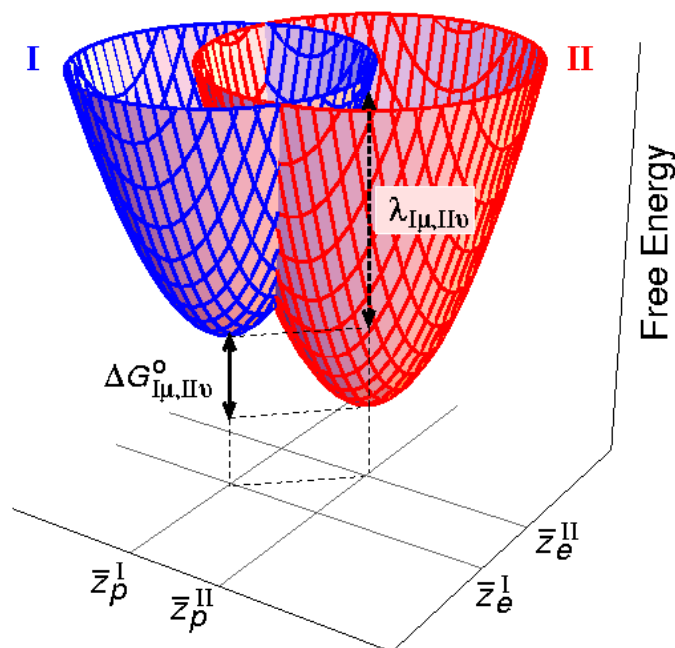
Reactant vibronic states: $\Phi^I(\mathbf{r}_e, \mathbf{r}_p) = \Psi_I(\mathbf{r}_e, \mathbf{r}_p) \varphi_{I\mu}(\mathbf{r}_p)$

Product vibronic states: $\Phi^{II}(\mathbf{r}_e, \mathbf{r}_p) = \Psi_{II}(\mathbf{r}_e, \mathbf{r}_p) \varphi_{II\nu}(\mathbf{r}_p)$

Coupling between reactant and product vibronic states typically much smaller than thermal energy because of small overlap → Describe reactions in terms of nonadiabatic transitions between reactant and product vibronic states

Vibronic states depend parametrically on other nuclear coords

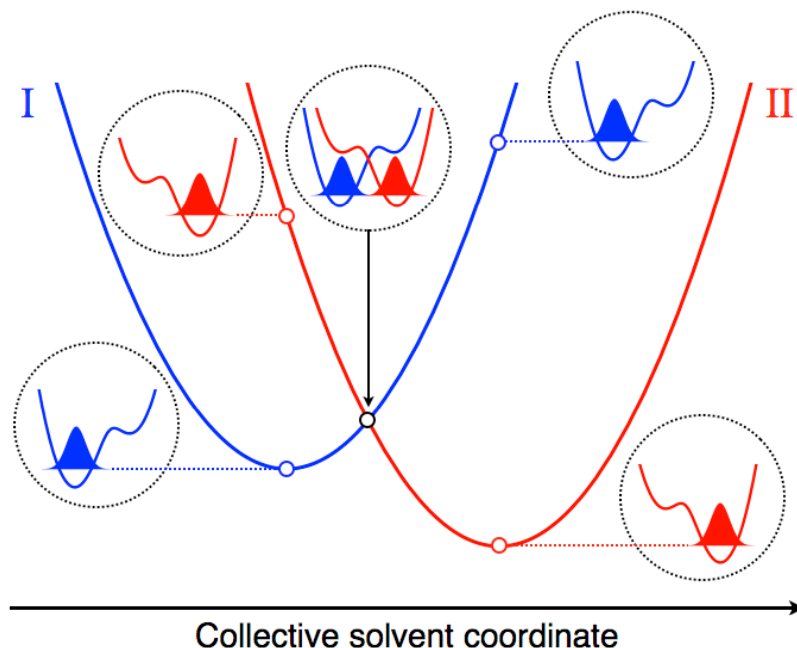
2D Vibronic Free Energy Surfaces



Reactant ($1a/1b$)	D^-	A
Product ($2a/2b$)	D	A^-

- Multistate continuum theory: free energy surfaces depend on 2 collective solvent coordinates, z_p (PT) and z_e (ET)
- Mixed electronic-proton vibrational (vibronic) surfaces
- Two sets of stacked paraboloids corresponding to different proton vibrational states for each electronic state

One-Dimensional Slices



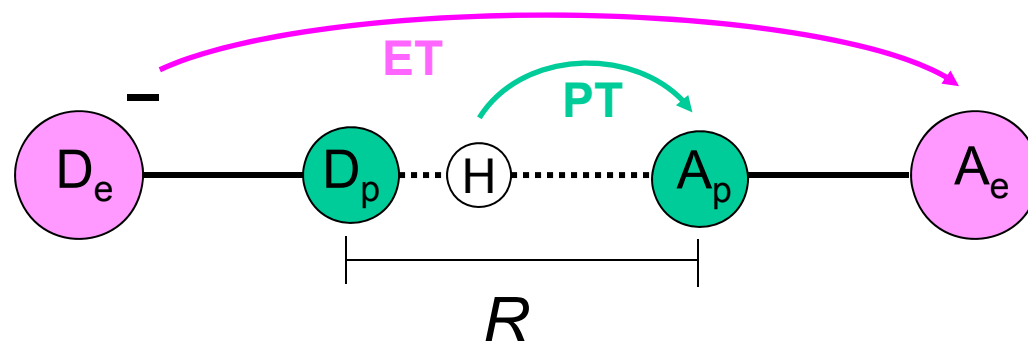
- Shape of proton potentials not significantly impacted by solvent coordinate in this range
- Relative energies of reactant and product proton potentials strongly impacted by solvent coordinate

Mechanism:

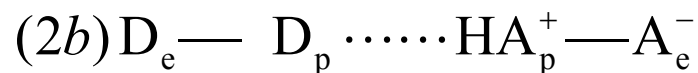
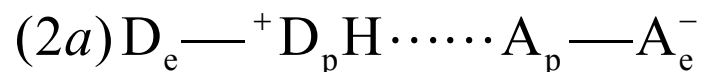
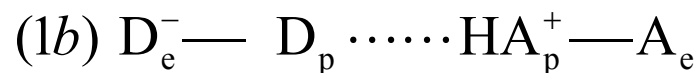
1. System starts in thermal equilibrium on **reactant surface**
2. Reorganization of solvent environment leads to crossing
3. Nonadiabatic transition to **product surface** occurs with probability proportional to square of vibronic coupling
4. Relaxation to thermal equilibrium on **product surface**

Overview of Theory for PCET

Hammes-Schiffer, Acc. Chem. Res. 34, 273 (2001)



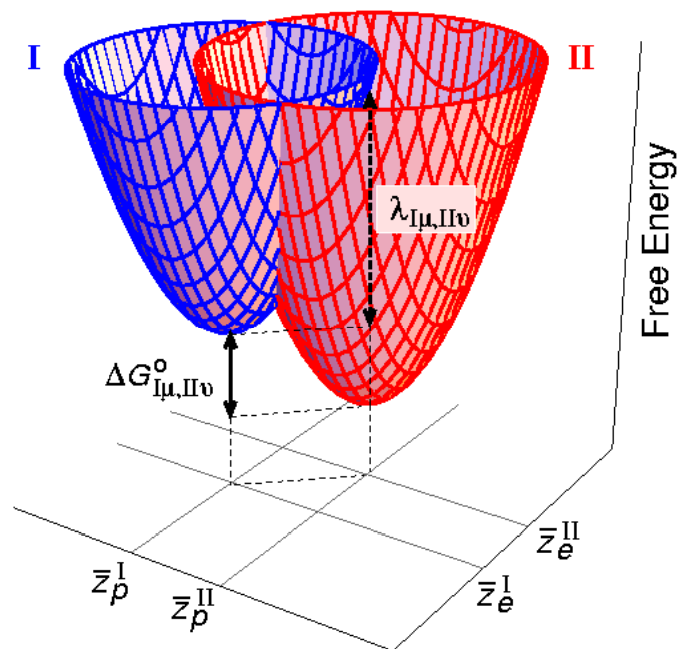
- Solute: 4-state model



- H nucleus: quantum mechanical wavefunction
- Solvent/protein: dielectric continuum or explicit molecules
- Typically nonadiabatic due to small coupling
- Nonadiabatic rate expressions derived from Golden Rule

PCET Rate Expression

Soudackov and Hammes-Schiffer, JCP 113, 2385 (2000)

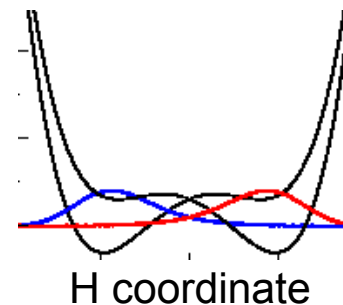


Reactant (1a/1b)	D ⁻	A
Product (2a/2b)	D	A ⁻

$$k = \frac{2\pi}{\hbar} \sum_{\mu} P_{\mu}^I \sum_{\nu} (4\pi\lambda_{\mu\nu}k_B T)^{-1/2} |V_{\mu\nu}|^2 \exp\left[-\Delta G_{\mu\nu}^{\dagger}/(k_B T)\right]$$

$$\Delta G_{\mu\nu}^{\dagger} = (\Delta G_{\mu\nu}^{\circ} + \lambda_{\mu\nu})^2 / (4\lambda_{\mu\nu})$$

$$V_{\mu\nu} = \left\langle \Phi^I(\mathbf{r}_e, \mathbf{r}_p) \left| \hat{H} \right| \Phi^{II}(\mathbf{r}_e, \mathbf{r}_p) \right\rangle \approx V^{\text{el}} S_{\mu\nu}$$

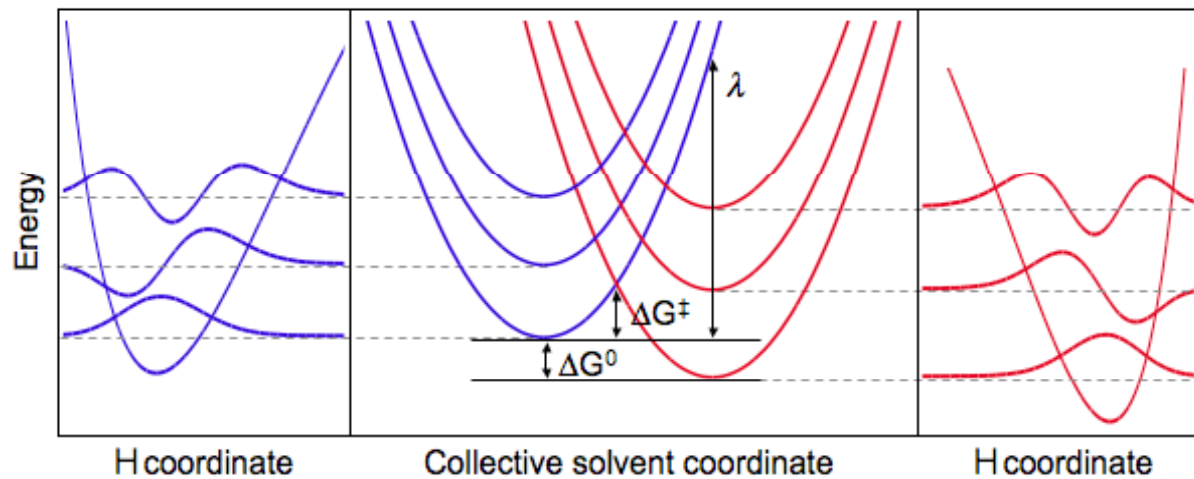


Excited Vibronic States

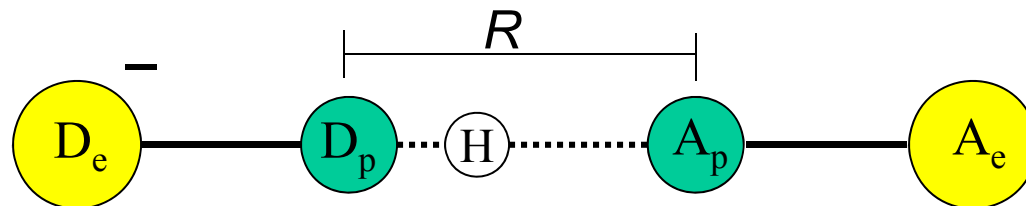
$$k = \frac{2\pi}{\hbar} \sum_{\mu} P_{\mu}^{\text{I}} \sum_{\nu} \left(4\pi\lambda_{\mu\nu} k_B T \right)^{-1/2} |V_{\mu\nu}|^2 \exp \left[-\Delta G_{\mu\nu}^{\ddagger} / (k_B T) \right]$$

Relative contributions from excited vibronic states determined from balance of factors (different for H and D, depends on T)

- Boltzmann probability of reactant state
- Free energy barrier
- Vibronic couplings (overlaps)

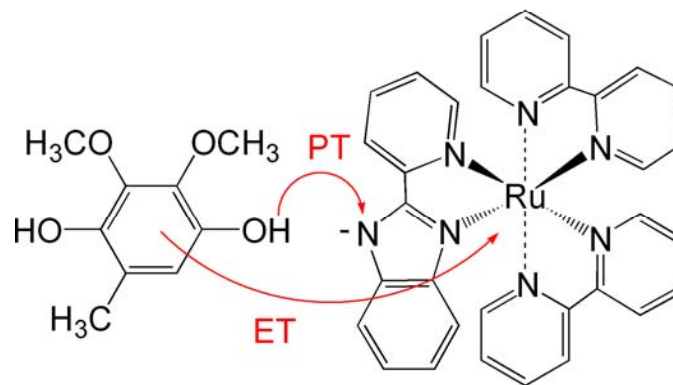


Proton Donor-Acceptor Motion

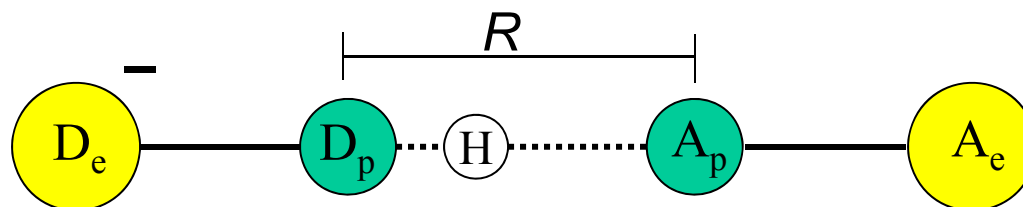


- R is distance between proton donor and acceptor atoms
- R -mode corresponds to the change in the distance R , typically at a hydrogen-bonding interface
- R -mode can be strongly influenced by other solute nuclei, viewed as the “effective” proton donor-acceptor mode
- PCET rate is much more sensitive to R than to electron donor-acceptor distance because of mass and length scales for PT compared to ET

For this PCET reaction, R is distance between donor O and acceptor N in PT reaction



Role of H Wavefunction Overlap



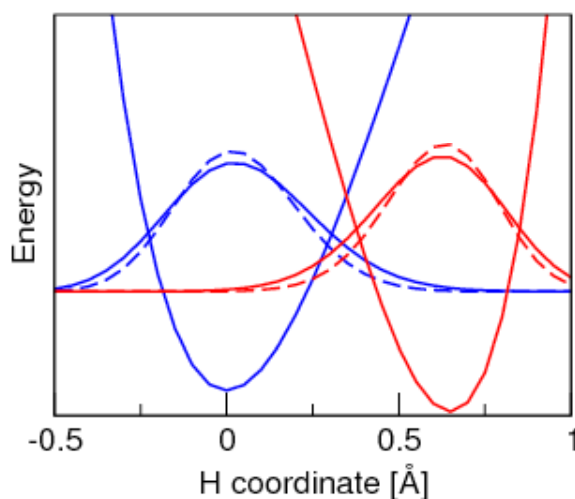
- Rate decreases as overlap decreases (as R increases)

$$k_H \propto V_H^2 \propto (H \text{ overlap})^2$$

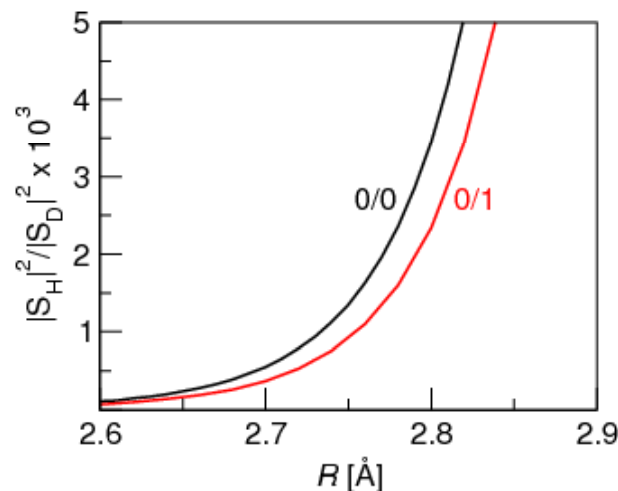
- KIE increases as overlap decreases (as R increases)

$$\frac{k_H}{k_D} \propto \frac{V_H^2}{V_D^2} \approx \frac{(H \text{ overlap})^2}{(D \text{ overlap})^2}$$

(for a pair of vibronic states)

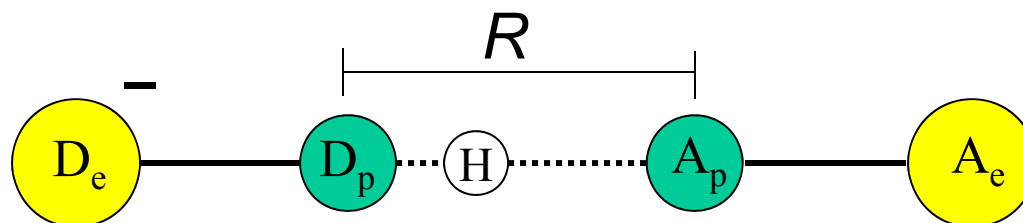


solid: H
dashed: D



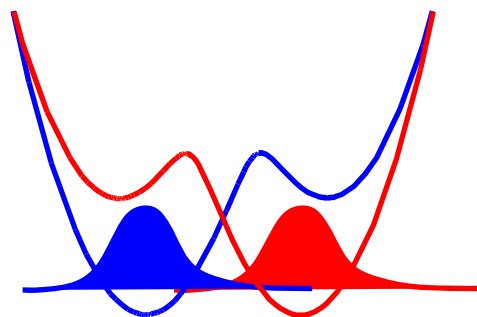
Include Proton Donor-Acceptor Motion

Soudackov, Hatcher, SHS, JCP 122, 014505 (2005)



- Vibronic coupling (overlap) depends strongly on R
- Approximate vibronic coupling as

$$V_{\mu\nu}(R) \approx V^{\text{el}} S_{\mu\nu}^0 \exp\left[-\alpha_{\mu\nu}(R - R_{\text{eq}})\right]$$



V^{el} : electronic coupling

$S_{\mu\nu}^0$: proton wavefunction overlap at R_{eq}

R_{eq} : equilibrium R value

- Derived dynamical rate constant with quantum R -mode and explicit solvent
- Derived approximate forms for low- and high-frequency R -mode using a series of well-defined approximations

Dynamical Rate for Molecular Environment

$$k_{\text{dyn}} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} j(t) dt$$

$$j(t) = |V^{\text{el}} S_{\mu\nu}^0|^2 \exp\left[\frac{i}{\hbar} \langle \mathcal{E} \rangle t\right] \\ \times \exp\left\{ \alpha^2 [C_R(0) + C_R(t)] - \frac{2i\alpha}{\hbar} \langle \tilde{D} \rangle \int_0^t C_R(\tau) d\tau \right. \\ \left. - \frac{1}{\hbar^2} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 C_{\mathcal{E}}(\tau_1 - \tau_2) - \frac{1}{\hbar^2} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 C_D(\tau_1 - \tau_2) C_R(\tau_1 - \tau_2) \right\}$$

Energy gap and its derivative: $\mathcal{E}(t) = \Delta\mathcal{E}(R_{\text{eq}}, \xi(t))$ $\tilde{D} = \left. \frac{\partial \Delta\mathcal{E}}{\partial R} \right|_{R=R_{\text{eq}}}$

Time correlation functions: $C_R(t)$, $C_{\mathcal{E}}(t)$, $C_D(t)$

- Calculate quantities with classical MD on reactant surface
- Includes explicit solvent/protein environment
- Includes dynamical effects of R -mode and solvent/protein

Soudackov, Hatcher, SHS, JCP 2005

Closed Analytical Rate Constant

Approximations: short-time, high-T limit for solvent and quantum harmonic oscillator *R*-mode

$$k = \sum_{\mu} P_{\mu}^{\text{I}} \sum_{\nu} \frac{|V^{\text{el}} S_{\mu\nu}^0|^2}{\hbar^2 \Omega} \exp\left[\frac{2\lambda_{\alpha}\zeta}{\hbar\Omega}\right] \int_{-\infty}^{\infty} d\tau \exp\left[-\chi\tau^2/2 + p(\cos\tau - 1) + i(q\sin\tau + \theta\tau)\right]$$

Parameters depend on T , reorganization energies, reaction free energies, vibronic coupling exponential factor, mass and frequency of *R*-mode, and difference in product and reactant equilibrium *R* values

Rate constant expressed in terms of physically meaningful parameters but requires numerical integration over time

High-Frequency R -mode

$$\Omega \gg k_B T$$

$$k = \sum_{\mu} P_{\mu}^I \sum_{\nu} \frac{|V^{\text{el}} S_{\mu\nu}^0|^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp \left[\frac{\lambda_{\alpha} - \lambda_R}{\hbar \Omega} - \alpha_{\mu\nu} \delta R \right] \exp \left[-\frac{(\Delta G_{\mu\nu}^0 + \lambda)^2}{4 \lambda k_B T} \right]$$

$$\lambda_{\alpha} = \frac{\hbar^2 \alpha_{\mu\nu}^2}{2M}$$

$$\delta R = M \Omega^2 \delta R^2 / 2$$

M, Ω : mass and frequency of R -mode

α : exponential R -dependence of vibronic coupling

δR : difference between product and reactant equilibrium values of R

Assumption of derivation (strong-solvation limit): $\lambda > |\Delta G_{\mu\nu}^0|$

In this limit, sole effect of R -mode on rate constant is that vibronic coupling is averaged over ground-state vibrational wavefunction of R -mode

For very high Ω , use fixed- R rate constant expression

Low-Frequency *R*-mode

$$\Omega \ll k_B T$$

$$k = \sum_{\mu} P_{\mu}^I \sum_{\nu} \frac{|V^{\text{el}} S_{\mu\nu}^0|^2}{\hbar} \exp\left[\frac{2k_B T \alpha_{\mu\nu}^2}{M \Omega^2}\right] \sqrt{\frac{\pi}{(\lambda + \lambda_{\alpha}) k_B T}} \exp\left[-\frac{(\Delta G_{\mu\nu}^0 + \lambda + \lambda_{\alpha})^2}{4(\lambda + \lambda_{\alpha}) k_B T}\right]$$

$$\lambda_{\alpha} = \frac{\hbar^2 \alpha_{\mu\nu}^2}{2M}$$

Typically $\lambda_{\alpha} \ll \lambda$

M, Ω : mass and frequency of *R*-mode

α : exponential *R*-dependence of vibronic coupling

Note: this expression assumes $\delta R = 0$; a more complete expression is available

Approximate KIE
(only ground states)

$$\text{KIE} \approx \frac{|S_H|^2}{|S_D|^2} \exp\left\{\frac{-2k_B T}{M \Omega^2} (\alpha_D^2 - \alpha_H^2)\right\}$$

- T-dependence of KIE determined mainly by α and Ω :
- KIE decreases with temperature because $\alpha_D > \alpha_H$
- Magnitude of KIE determined also by ratio of overlaps:
smaller overlap \rightarrow larger KIE

Reorganization Energies

- Reorganization energy λ in previous expressions refers to **solvent/protein reorganization energy** (outer-sphere)
- **Inner-sphere reorganization energy** (intramolecular solute modes) can also be included
 - high-T limit (low-frequency modes): add inner-sphere reorganization energy to solvent reorganization energy
 - low-T limit (high-frequency modes): modified rate constant expression has been derived
(Soudackov and Hammes-Schiffer, JCP 2000)
- **Calculation of reorganization energies**
 - Outer-sphere: dielectric continuum models or molecular dynamics simulations
 - Inner-sphere: quantum mechanical calculations on solute

Input Quantities

- Reorganization energies (λ)
 - outer-sphere (solvent): dielectric continuum model or MD
 - inner-sphere (solute modes): QM calculations of solute
 - Free energy of reaction for ground states (driving force) (ΔG^0)
 - QM calculations or estimate from pK_a 's and redox potentials
 - *R*-mode mass and frequency (M, Ω)
 - QM calculation of normal modes or MD
 - *R*-mode is dominant mode that changes proton donor-acceptor distance
 - Proton vibrational wavefunction overlaps ($S_{\mu\nu}, \alpha_{\mu\nu}$)
 - approximate proton potentials with harmonic/Morse potentials or generate with QM methods
 - numerically calculate H vibrational wavefunctions w/ Fourier grid methods
 - Electronic coupling (V^{el})
 - QM calculations of electronic matrix element or splitting
- Note: this is a multiplicative factor that cancels for KIE calculations

Warnings about Prediction of Trends

Edwards, Soudackov, SHS, JPC A113, 2117 (2009)

- Experimentally challenging to change only a single parameter

Examples:

Increasing R often decreases Ω ; may impact KIE in opposite way

Changing driving force by altering pK_a can also impact R

- Relative contributions from pairs of vibronic states are sensitive to parameters, H vs. D , and temperature

Must perform full calculation (converging number of reactant and product vibronic states) to predict trend

- High-frequency and low-frequency R -mode rate constants are qualitatively different

Example:

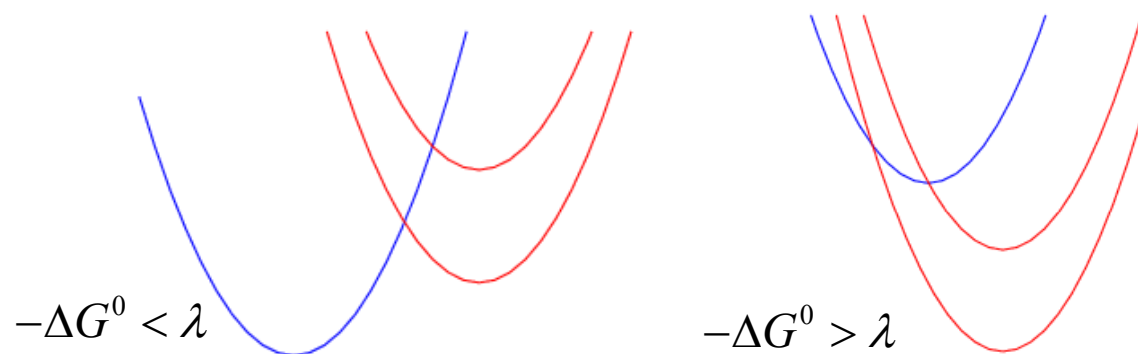
Low-frequency expression predicts KIE decreases with T

Fixed- R and high-frequency expressions can lead to either increase or decrease of KIE with T

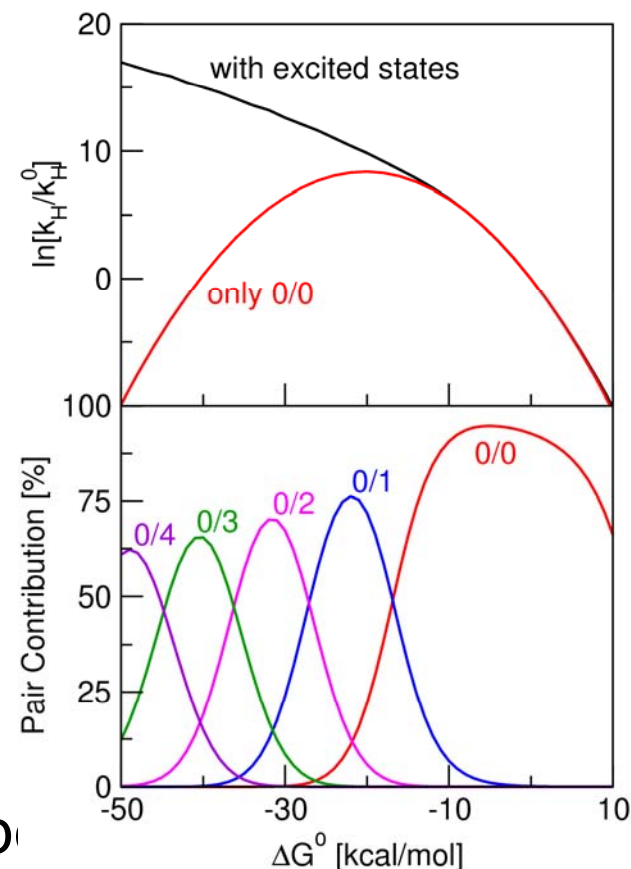
Driving Force Dependence

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

Free energy vs. Solvent coordinate



- Theory predicts inverted region behavior not experimentally accessible for PCET due to excited vibronic states with enhanced couplings
- Apparent inverted region behavior could be observed experimentally if changing driving force also impacts other parameters (e.g., increasing $|\Delta pK_a|$ also increases R)

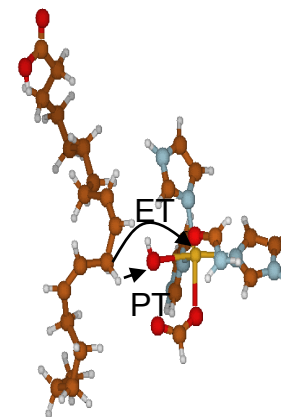
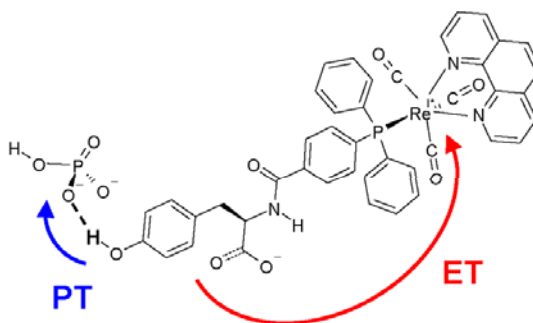
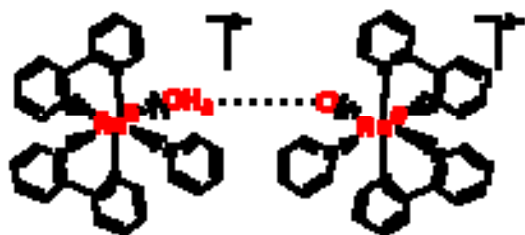


Applications to PCET Reactions

- 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, 2007
- Rhenium-tyrosine complex (Nocera), *JACS* 2007
- Quinol oxidation (Kramer), *JACS* 2009
- Osmium aquo complex/SAM/gold electrode (Finklea), *JACS* 2010

Experimental groups in parentheses, followed by journal and year of Hammes-Schiffer group application

Theory explained experimental trends in rates, KIEs, T-dependence, pH-dependence



Distinguishing between HAT and PCET

Skone, Soudackov, SHS, JACS 128, 16655 (2006)

- Overall HAT and PCET usually *vibronically nonadiabatic* since vibronic coupling much less than thermal energy: $V_{\mu\nu} \ll k_B T$
- PT can be electronically nonadiabatic, adiabatic, or in between, depending on relative timescales of electronic transition (τ_e) and proton tunneling (τ_p)
 - electronically adiabatic PT: electrons respond instantaneously to proton motion, $\tau_e \ll \tau_p$
 - electronically nonadiabatic PT: electrons do not respond instantaneously, $\tau_e \gg \tau_p$
- HAT \leftrightarrow electronically adiabatic PT
- PCET \leftrightarrow electronically nonadiabatic PT

Quantify Nonadiabaticity: Vibronic Coupling

Georgievskii and Stuchebrukhov, JCP 2000; Skone, Soudackov, SHS, JACS 2006

$$V_{DA}^{(\text{sc})} = \kappa V_{DA}^{(\text{ad})}$$

$$\kappa = \sqrt{2\pi p} \frac{e^{p \ln p - p}}{\Gamma(p+1)}$$

$$p = \frac{|V^{\text{el}}|^2}{\hbar |\Delta F| v_t} = \frac{\tau_p}{\tau_e}$$

$$\tau_e \approx \frac{\hbar}{V^{\text{el}}} \quad \tau_p \approx \frac{|V^{\text{el}}|}{|\Delta F| v_t}$$

$$v_t = \sqrt{\frac{2(V_c - E)}{m}}$$

V_c : energy at crossing point

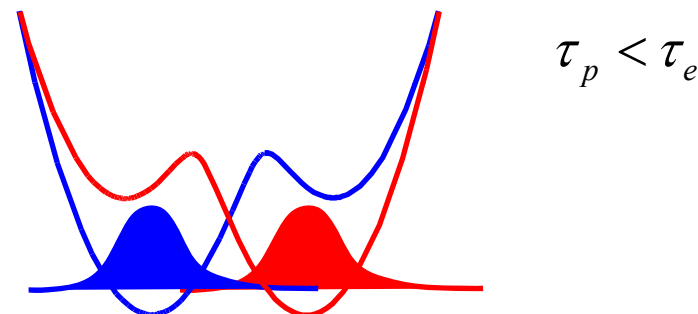
E : tunneling energy (vibrational ground state)

$|\Delta F|$: difference of slopes of potential energy curves

V^{el} : electronic coupling

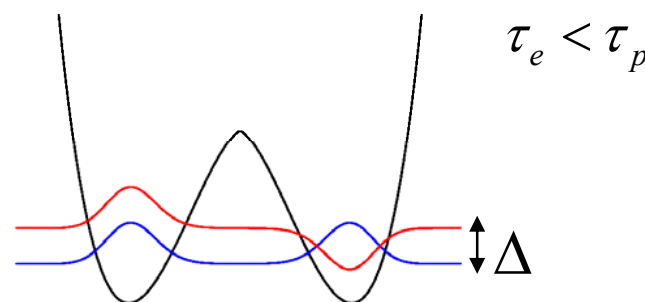
Electronically nonadiabatic PT: $\kappa \approx \sqrt{2\pi p}$, $p \ll 1$,

$$V_{DA}^{(\text{na})} = V^{\text{el}} \langle \varphi_D^{(1)} | \varphi_A^{(2)} \rangle$$



Electronically adiabatic PT: $\kappa \approx 1$, $p \gg 1$

$$V_{DA}^{(\text{ad})} = \Delta / 2$$



Representative Chemical Examples

Phenoxy/Phenol and Benzyl/Toluene self-exchange reactions

DFT calculations and orbital analysis:

Mayer, Hrovat, Thomas, Borden, JACS 2002

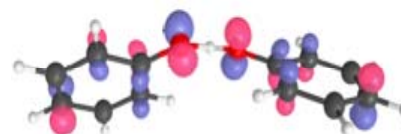
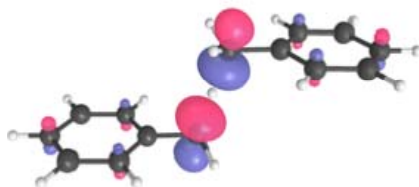
benzyl/toluene

C---H---C

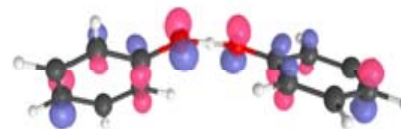
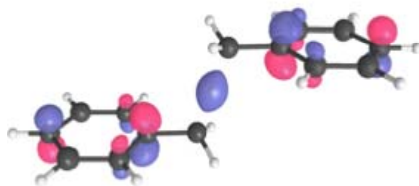
phenoxy/phenol

O---H---O

SOMO



DOMO



HAT

*ET and PT between
same orbitals*

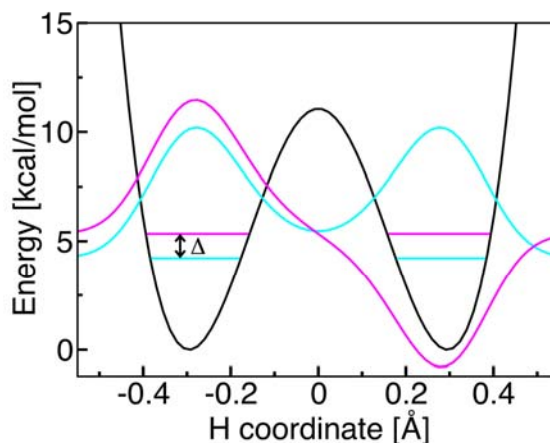
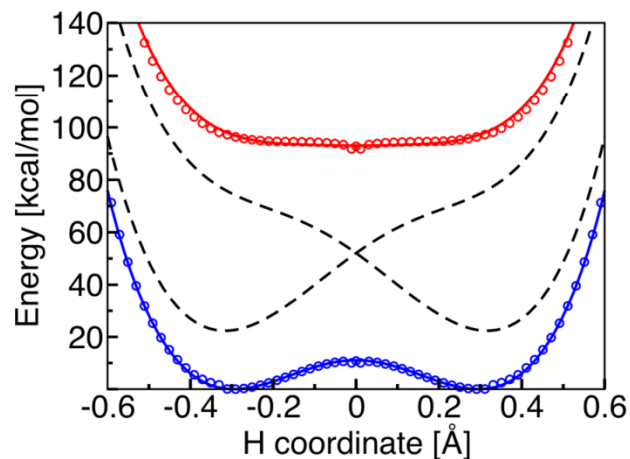
PCET

*ET and PT between
different orbitals*

PCET vs. HAT: Adiabaticity Parameter

Skone, Soudackov, SHS, JACS 2006

Benzyl-toluene: C---H---C, electronically adiabatic PT, HAT

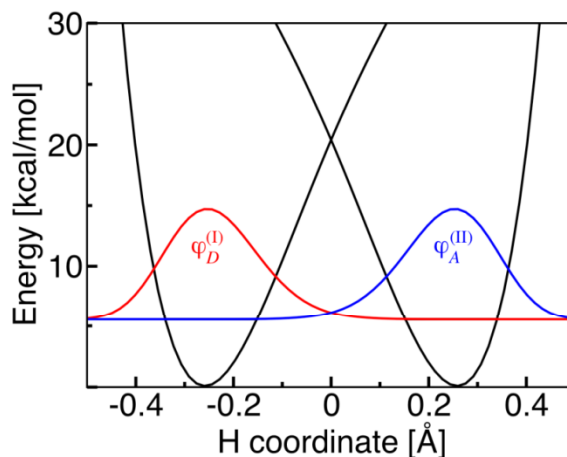
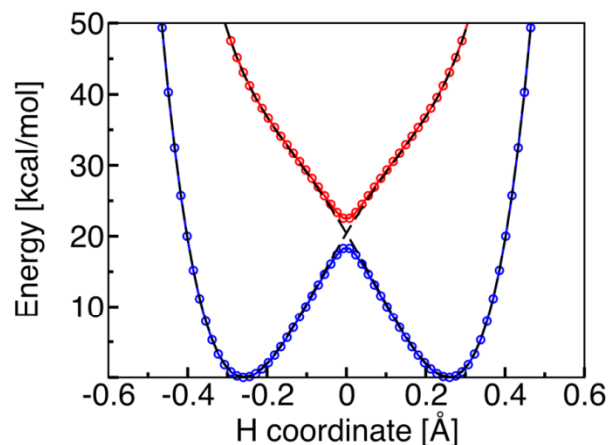


$$p \approx 4, \quad \tau_p \approx 4\tau_e$$

$$V^{\text{el}} = 14,000 \text{ cm}^{-1}$$

$$V_{DA}^{(\text{sc})} \approx V_{DA}^{(\text{ad})} = \Delta/2$$

Phenoxyl-phenol: O---H---O, electronically nonadiabatic PT, PCET



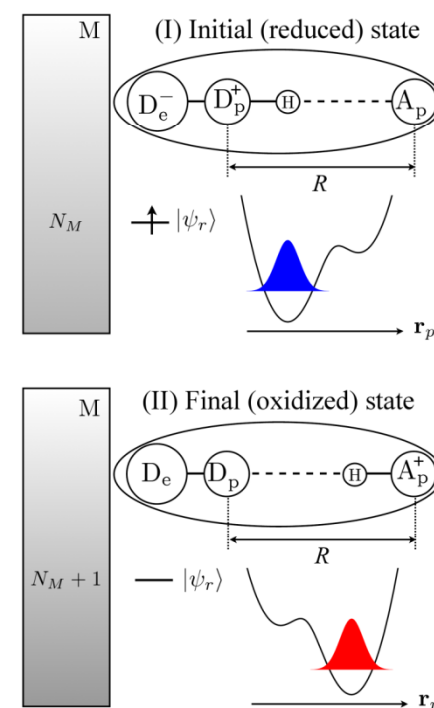
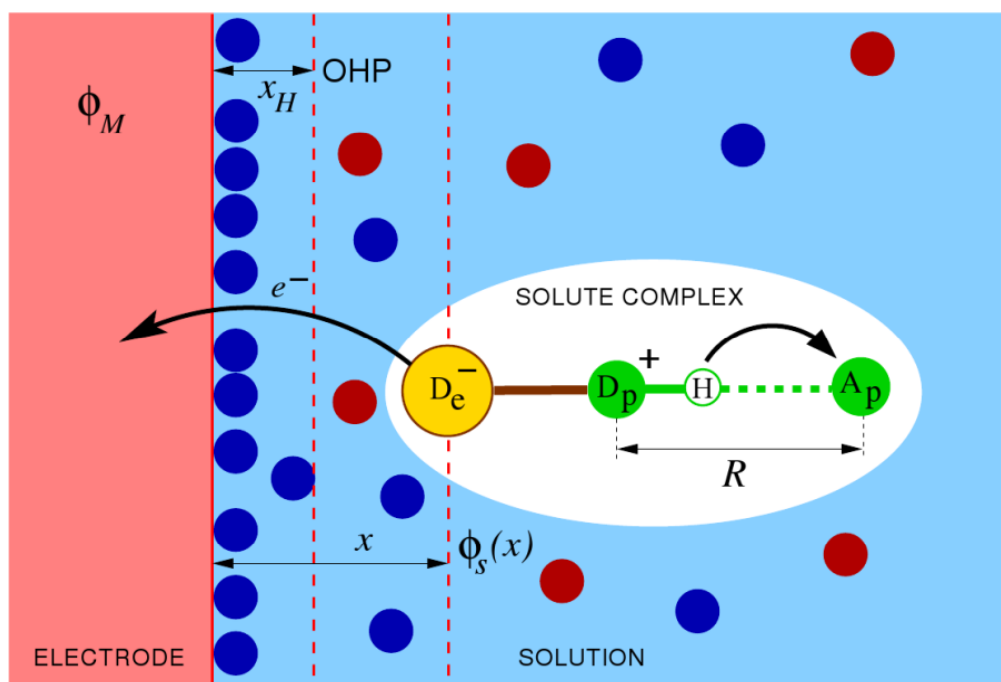
$$p \approx 0.01, \quad \tau_e \approx 80\tau_p$$

$$V^{\text{el}} = 700 \text{ cm}^{-1}$$

$$V_{DA}^{(\text{sc})} \approx V_{DA}^{(\text{na})} = V^{\text{el}} \langle \varphi_D^{(1)} | \varphi_A^{(2)} \rangle$$

Electrochemical PCET Theory

Venkataraman, Soudackov, SHS, JPC C 112, 12386 (2008)



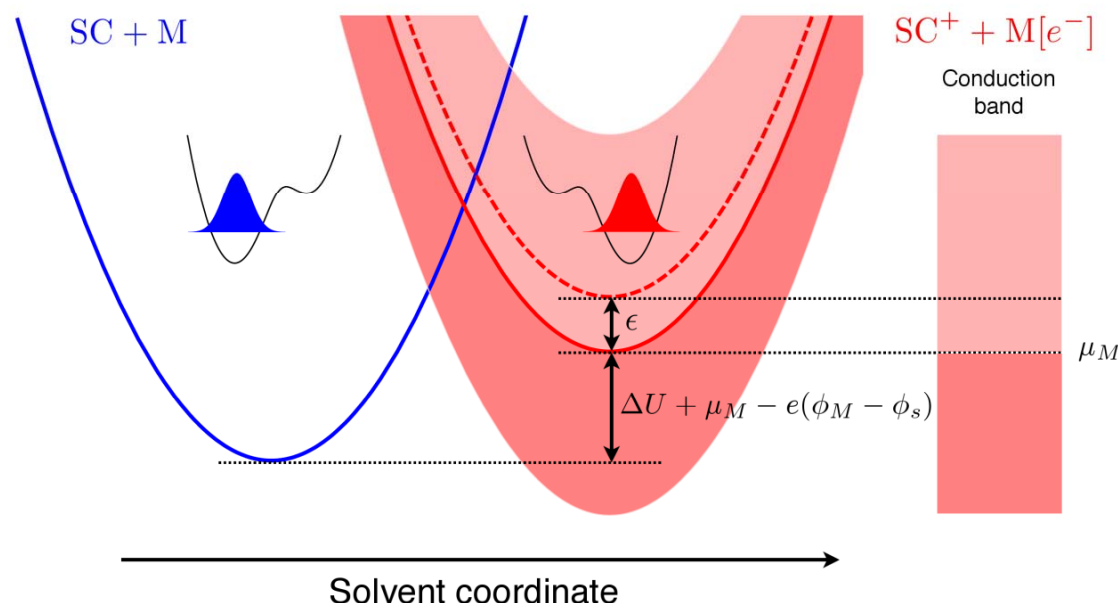
Derived expressions for current densities $j(\eta)$

- Current densities obtained by explicit integration over x

$$j_a = F \int_{x_H}^{\infty} dx C_{SC}(x) k_a(x)$$

- Gouy-Chapman-Stern model for double layer effects

Rate Constants for Electrochemical PCET



- Nonadiabatic transitions between electron-proton vibronic states
- Integrate transition probability over ϵ , weighting by Fermi distribution and density of states for metal electrode

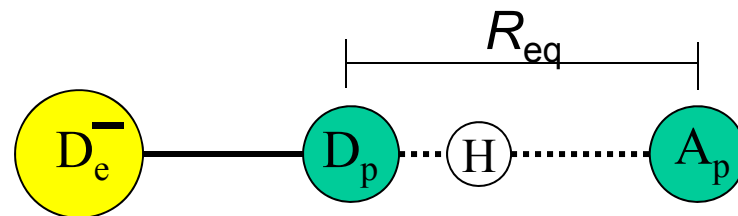
$$k_a(x) = \int d\epsilon [1 - f(\epsilon)] \rho(\epsilon) W_a(x, \epsilon)$$

- Similar transition probabilities with modified reaction free energy:

$$\Delta G_{\mu\nu}(x, \epsilon) \approx \Delta U_{\mu\nu} - \Delta U_{00} + \epsilon - e\eta + e\phi_s(x)$$

Characteristics of Electrochemical PCET

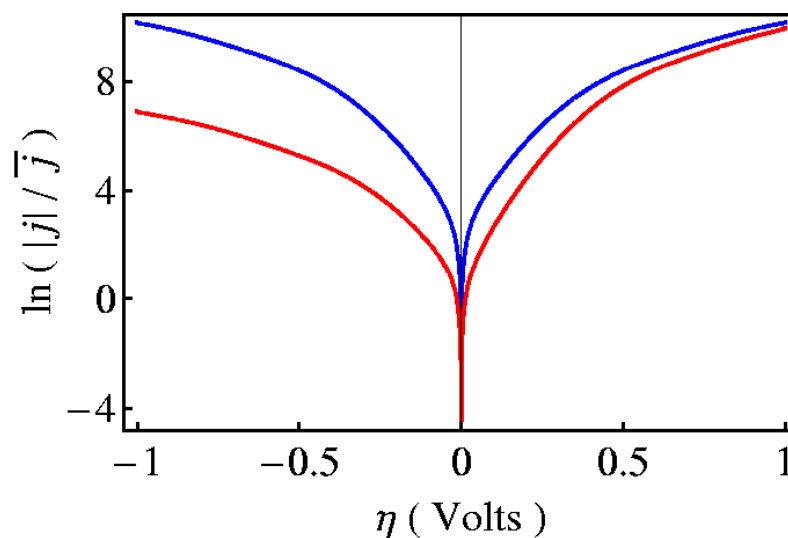
- pH dependence: buffer titration, kinetic complexity, H-bonding
- Kinetic isotope effects
- Non-Arrhenius behavior at high T
- Asymmetries in Tafel plots, $\alpha_T \neq 0.5$ at $\eta=0$ (observed experimentally)



$$\delta R_{eq} = 0$$

$$\delta R_{eq} = 0.05 \text{ \AA}$$

Effective activation energy contains T-dependent terms $\pm 2\alpha_{\mu\nu}\delta R_{eq}k_B T$ due to change in R_{eq} upon ET; different sign for cathodic and anodic processes \rightarrow asymmetries in Tafel plots



Cathodic transfer coefficient:

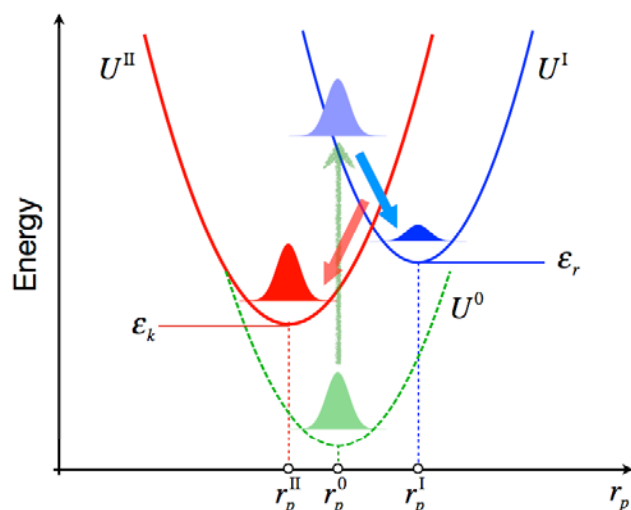
$$\alpha_T(\eta = 0) \approx 0.5 - \alpha_{00}\delta R_{eq}k_B T / \Lambda_{00}$$

Venkataraman, Soudackov, SHS, JPC C 2008

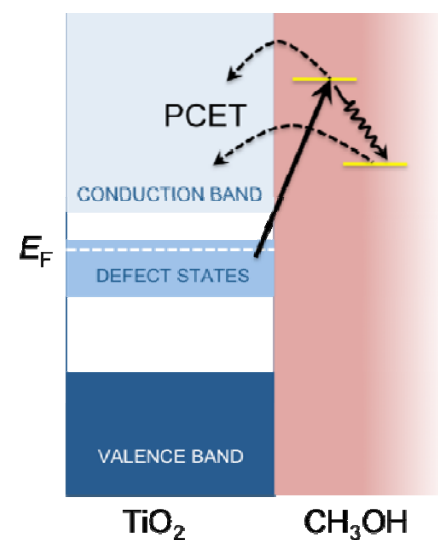
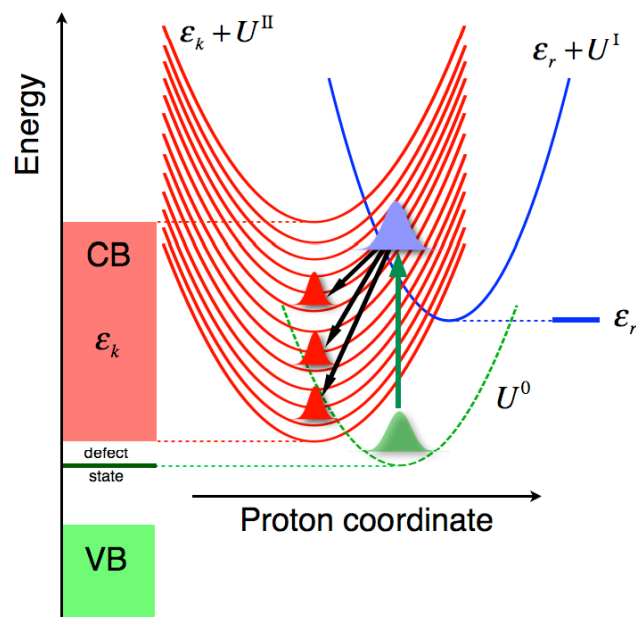
Photoinduced PCET

Venkataraman, Soudackov, SHS, JCP 131, 154502; JPC C 114, 487 (2009)

Homogeneous



Interfacial: molecule-semiconductor interface



- Developed model Hamiltonian
- Derived equations of motion for reduced density matrix elements in electron-proton vibronic basis
- Enables study of ultrafast dynamics in photoinduced processes

Beyond the Golden Rule

Navrotskaya and Hammes-Schiffer, JCP 131, 024112 (2009)

- Derived rate constant expressions that interpolate between golden rule and solvent-controlled limits
- Includes effects of solvent dynamics
- Golden rule limit
 - weak vibronic coupling, fast solvent relaxation
 - rate constant proportional to square of vibronic coupling, independent of solvent relaxation time
- Solvent-controlled limit
 - strong vibronic coupling, slow solvent relaxation
 - rate constant independent of vibronic coupling, increases as solvent relaxation time decreases
- Interconvert between limits by altering physical parameters
- KIE behaves differently in two limits, provides unique probe

webPCET

<http://webpcet.chem.psu.edu>

- Interactive Java applets allow users to perform calculations on model PCET systems and visualize results
- Harmonic, Morse, or general proton potentials
- “Exact”, fixed R , low-frequency or high-frequency R -mode rate constant expressions
- Plot dependence of rates and KIEs as function of temperature and driving force
- Analyze contributions of vibronic states
- Access via free registration

webPCET Portal

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