

The Abdus Salam International Centre for Theoretical Physics



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Workshop on New Materials for Renewable Energy

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Theoretical modeling of proton-coupled electron transfer reactions in energy related materials

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### II. Non-equilibrium dynamics of photoinduced proton-coupled electron transfer PENNSTATE Ander V. Soudackov Pennsylvania State University

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

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State College, PA,

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# Outline

- Experimental systems
- Proton vibrational dynamics in interfacial PCET
  - simulations of quantum dynamics with RDM approach
  - dynamics and isotope effects in model systems
- Quantum-classical dynamics of PCET involving solvent relaxation
  - solvent classical dynamics in the uniform continuum model
  - short time scale issues
  - how do we apply theory to model real systems
- Future directions

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- fast: <30 fs (polaron formation or surface Ti-O relaxation?)
- slow: up to ps range, depends on coverage (solvent relaxation?)
- no slow component for low coverages (< 1 ML)





# PCET Dynamics via RDM Approach

Second order perturbation theory for weak (renormalized) interaction and strong system-bath coupling: Markovian master equations for reduced density matrix (RDM)

$$\hat{A}_{rm,rm}(t) = \hat{A} W_{rm,kn}(t) s_{kn,kn}(t) - \hat{A} W_{kn,rm}(t) s_{rm,rm}(t)$$

$$\hat{A} W_{kn,rm}(t) s_{rm,rm}(t) - \hat{A} W_{rm,kn}(t) s_{kn,kn}(t)$$

Transition probabilities:  $W_{rmkn} = \frac{1}{h^2} |V_{rk}|^2 S_{mn}^2 \left[ \int_{0}^{\bullet} dt \, e^{i(\hat{U} - \hat{U}_k + E_m^{\dagger} E_n^{\dagger})t/h} e^{\hat{v}(t)} e^{-\hat{v}(0)} \hat{C} \right]$  $W_{kn,rm} = \frac{1}{h^2} |V_{rk}|^2 S_{mn}^2 \left[ \int_{0}^{\bullet} dt \, e^{i(\hat{U} - \hat{U}_k + E_m^{\dagger} E_n^{\dagger})t/h} e^{\hat{v}(t)} e^{-\hat{v}(0)} \hat{O} \right]$ 

#### Approximations:

- fast bath relaxation (bath is always at equilibrium) Markovian dynamics
- discretized electronic states in the conduction band of semiconductor
- no direct proton vibrational relaxation (usually much slower) only through PCET transitions

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- Multiple PCET transitions among highly excited vibronic states (with coherent proton wave packet) – NO ISOTOPE EFFECT – femtosecond timescale
- PCET transitions among lower vibronic states (strong dephasing) – PRONOUNCED ISOTOPE EFFECT – picosecond timescale

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$$\frac{1}{18} \frac{1}{12} \frac{1}{12} \frac{1}{12} V_{a} = \frac{1}{18} \frac{$$

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## **PSII** biomimetic systems

Photoinduced EPT in hydrogen bonded base adducts with 4-nitro-4'-biphenylphenol



Gagliardi , Westlake, Kent, Paul, Papanikolas, Meyer, Coord. Chem. Rev., 254, 2459, (2010)

- initial charge transfer  $(n\pi^*)$  excitation prepares the proton in highly excited vibrational states
- pump 388 nm: EPT in the excited state
  - relaxation occurs on a subps timescale (~200 fs) and involves coupled proton vibrational and solvent modes





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- initial charge transfer  $(n\pi^*)$  excitation prepares the proton in highly excited vibrational states
- pump 388 nm: EPT in the excited state
  - relaxation occurs on a subps timescale (~200 fs) and involves coupled proton vibrational and solvent modes
- pump 355 nm: excited state PT after vibrational and solvent relaxation (ps timescale)















### Interaction with polar solvent

Vibronic free energy surfaces

- Generalized Marcus model
  - polarization field P(r) can be rigorously mapped onto scalar solvent coordinate(s) – differences in interaction energies ("Zusman energy gap coordinate(s)").
  - electron-proton vibronic Hamiltonian parametrically depends on solvent coordinate(s) – diagonalization provides vibronic free energy surfaces

$$U_n(Z_p, Z_e) = S(Z_p, Z_e) + W_n(Z_p, Z_e)$$

free energy of self (free) energy of the vibronic energy including n-th vibronic state polarization field solute-solvent interaction (depends on reorganization energies) (the vibronic energy including solute-solvent interaction)

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





### Solvent dynamics

How system evolves on free energy vibronic surfaces









How system evolves on free energy vibronic surfaces

Onodera model of dielectric relaxation  $\rightarrow$  ordinary Langevin equations:

$$\frac{f_0 t_0 t_1 z(t) = -f_0 \psi z_1 t) - --W_n - f_0 z + F(t)}{\sqrt{2}}$$

Acceleration term Friction (with effective mass) force



Random force

Solvent parameters from solvent dielectric function

- longitudinal dielectric relaxation time  $\tau_{L^{=}}$   $\epsilon_{\infty}\tau_{D}/\epsilon_{0}$
- short time rotational relaxation period  $\tau_{\rm O}$

(from molecular moment of inertia)

• dielectric constants  $\varepsilon_0, \varepsilon_\infty$ ; inverse Pekar factor

$$e(w) = e_{\bullet} + \frac{e_{0} - e_{\bullet}}{(1 - iwt_{D})(1 - iwt_{O})}$$

$$f_0^{-1} = \frac{1}{4p} \frac{E_0^{-1}}{E_0^{-1}} - \frac{1}{e_0^{-1}}$$

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### How system evolves on free energy vibronic surfaces

Mixed quantum-classical nonadiabatic dynamics: Tully's Fewest Switches Surface Hopping



- classical trajectories along solvent coordinates evolve on the adiabatic surfaces
- quantum amplitudes are propagated by solving TDSE (between classical timesteps)
- trajectories are allowed to "hop" or "switch" between surfaces (with probabilities depending on the magnitude and direction of the nonadiabatic coupling vector d<sub>mn</sub>)

• swarm of trajectories is propagated in time and the time-dependent Tuesday 25 October 2011







#### Type A

- solvent out of equilibrium with respect to ET (shift along  $Z_e$  coordinate)
- proton vibrational wavepacket ground vibrational state of 1a electronic state

#### Type B

- solvent out of equilibrium with respect to both ET and PT (shift along  $Z_e$  and  $Z_p$  coordinates)
- proton vibrational wavepacket shifted towards 1b state (coherent mixture of vibrational states of 1a electronic state)



- at *t* = 0: coherent mixture of vibrationally excited states (proton is shifted) and solvent highly out of equilibrium
- at  $t = \infty$ : ground vibronic state with equal populations of 1a and 2b minima







### Simulation results

Combination of EPT and ETPT: Collinear PCET model IA with bias



- at *t* = 0: Higher excited vibronic states and solvent highly out of equilibrium
- at  $t = \infty$ : 1-st excited vibronic state with entire population in 2b minimum (bias)





- Mechanism (combination of EPT and sequential ETPT)
  - during initial 3 ps: combination of ET (1a $\rightarrow$ 2a) and EPT (1a $\rightarrow$ 2b) in excited states
  - following ~20 ps: combination of PT (2a $\rightarrow$ 2b) and proton vibrational relaxation



### Simulation results

### Sequential ETPT: Orthogonal PCET model IIA



- at t = 0: ground and 1-st excited vibronic states; solvent out of equilibrium along along ET solvent coordinate
- at  $t = \infty$ : ground vibronic state with equal populations in all 4 minima





- Mechanism (sequential: fast nonadiabatic ET followed by slower adiabatic PT)
  - during initial 200 fs: fast nonadiabatic ET (1a $\rightarrow$ 2a) and relaxation to ground state
  - following ~10 ps: adiabatic (over-the-barrier) PT ( $1a \rightarrow 1b$  and  $2a \rightarrow 2b$ )

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- at t = 0: higher excited vibronic states (coherent mixture due to proton shift); solvent out of equilibrium along along both ET and PT solvent coordinates
- at  $t = \infty$ : ground vibronic state with equal populations in all 4 minima





- Mechanism (highly collective with branching)
  - initial ~1 ps: fast relaxation to the central region of strong nonadiabatic couplings
  - following ~10 ps: multiple nonadiabatic transitions down the central funnel



- model with single relaxation period may not be good enough for most of the dipolar solvents (as demonstrated by MD simulations and experiment)
- may be missing short relaxation timescale associated with fast motions in the first solvation shell
- practical implementation of solvent dynamics is restricted to Debye-like models of dielectric relaxation with maximum of two relaxation periods

### Molecular solvent model





Ben Auer

Work in the final stages (Ben Auer)...

- 4-state EVB [A. Warshel] for PCET reaction complex + explicit molecular solvent
- adiabatic vibronic states are obtained by quantization of the proton on the fly
- surface hopping with classical dynamics on the adiabatic vibronic surfaces (with Hellman-Feynman forces calculated on the fly)

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### Future directions

- Implementation of models with multiple relaxation time scales
- Applications to real systems: T. Meyer's experiments
  - need accurate gas-phase surfaces for excited states (work in progress -Brian Solis in collaboration with Massimo Olivucci, Universita di Siena)



Brian Solis



Massimo Olivucci



