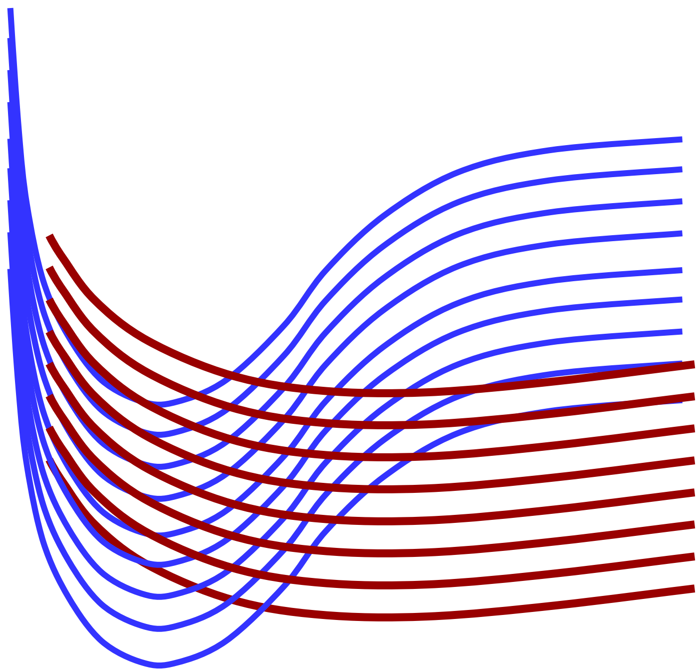
KAVLI ITP November 2 – 6, 2009

Dynamics at Metal Surfaces: Electronic Excitations

Sharani Roy

Emphasis:

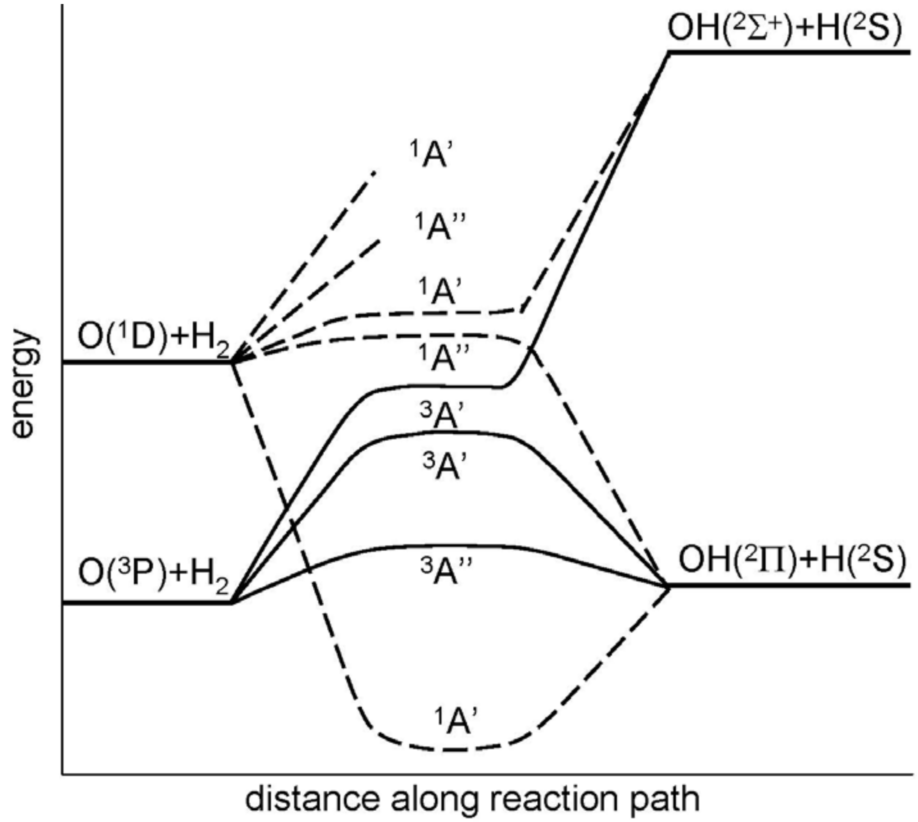
- open-shell adsorbates
- electron transfer
- multiple potential energy surfaces



Neil Shenvi

Reactions of open shell atoms and molecules in the gas phase

$O(^3P) + H_2 \rightarrow OH + H$



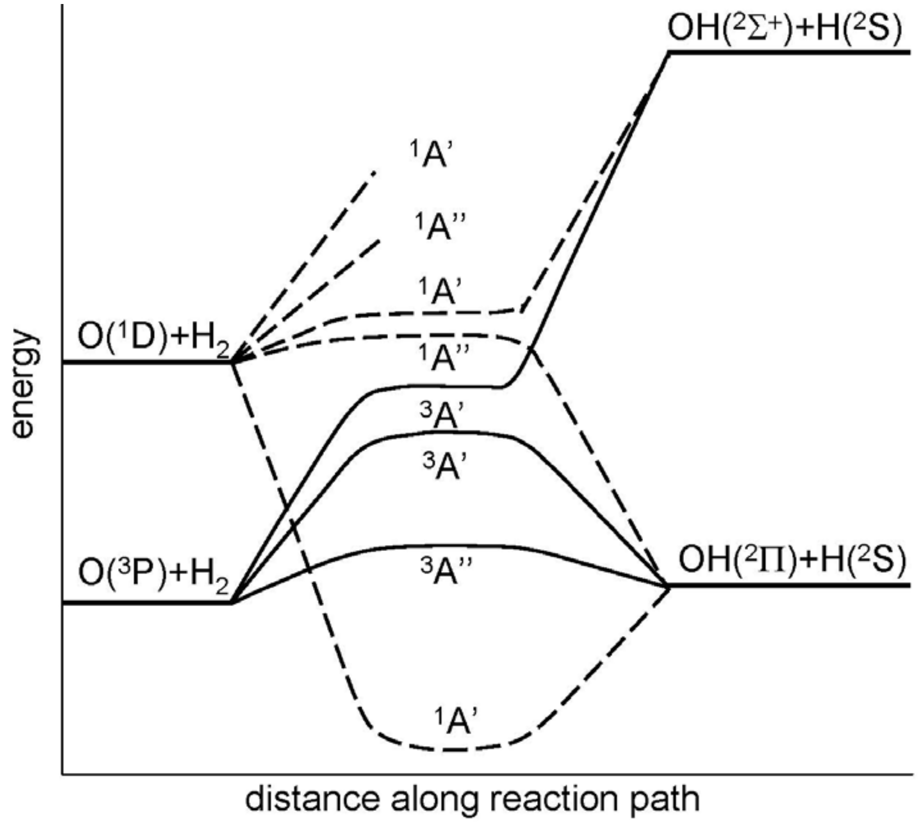
Challenges:

- Compute excited state potential energy surfaces plus nonadiabatic and spin-orbit couplings

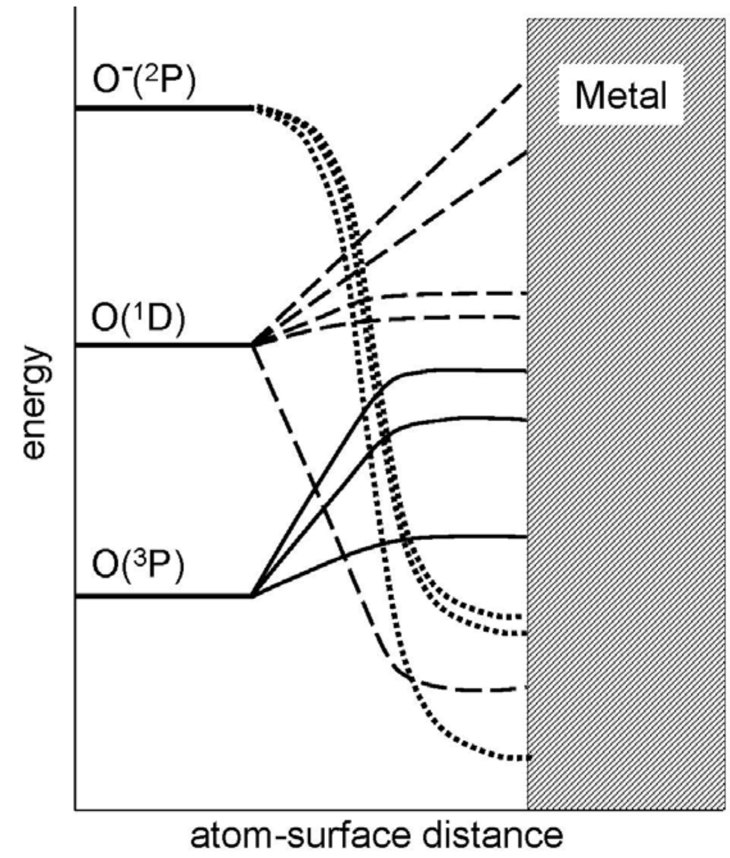
2. Propagate ion motion subject to multiple potential energy surfaces

Reactions of open shell atoms and molecules at surfaces

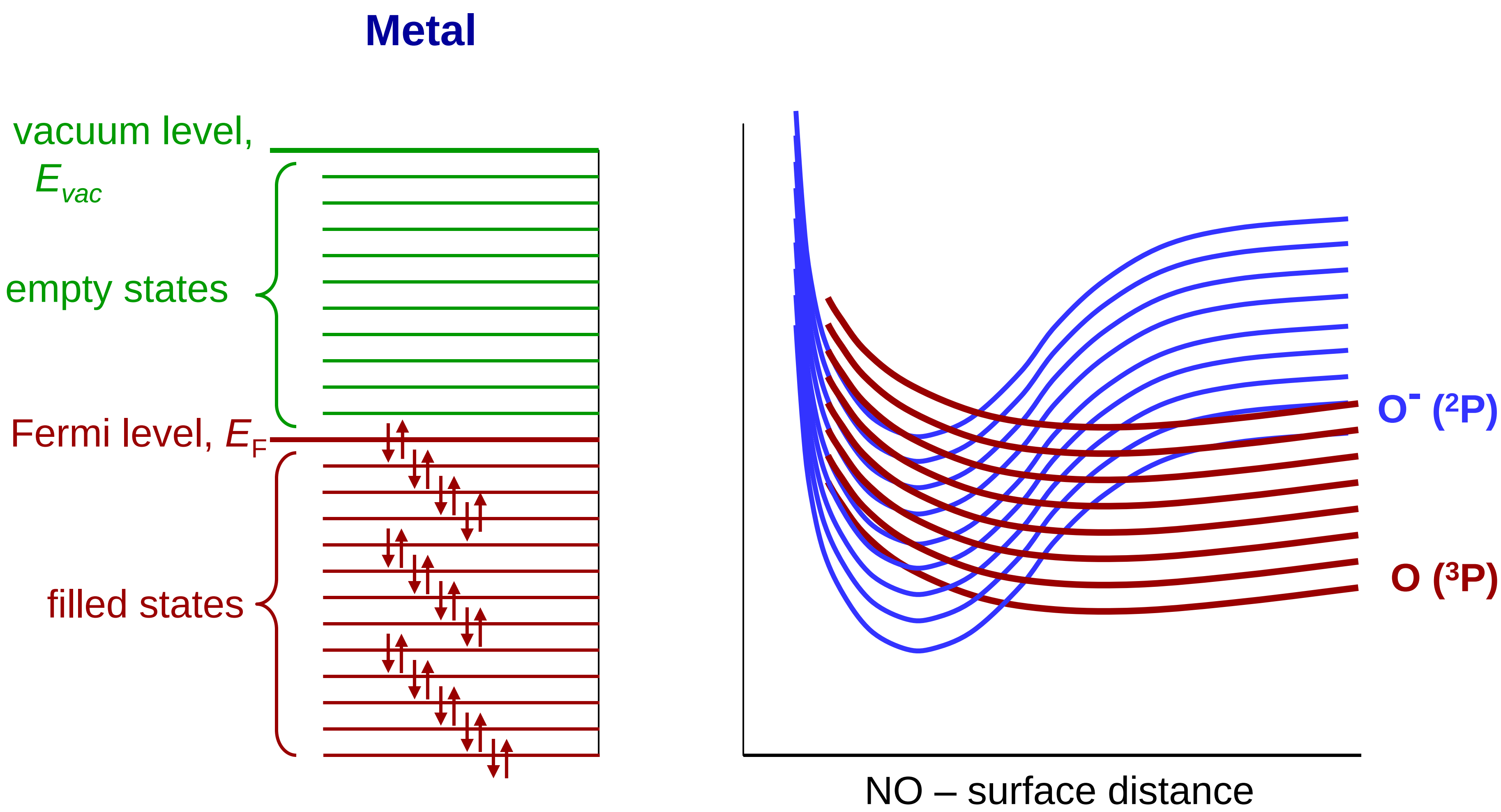
Gas Phase

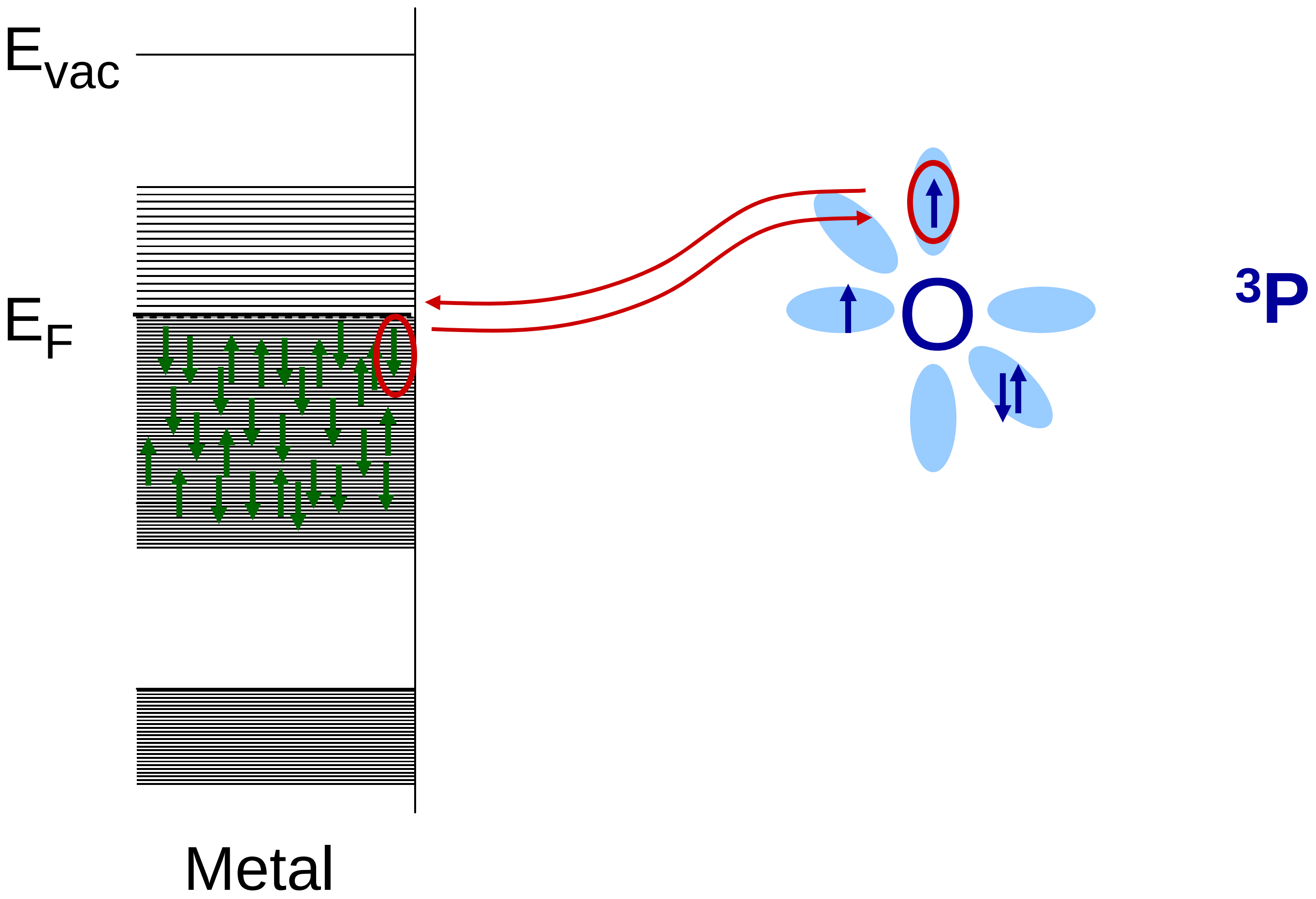


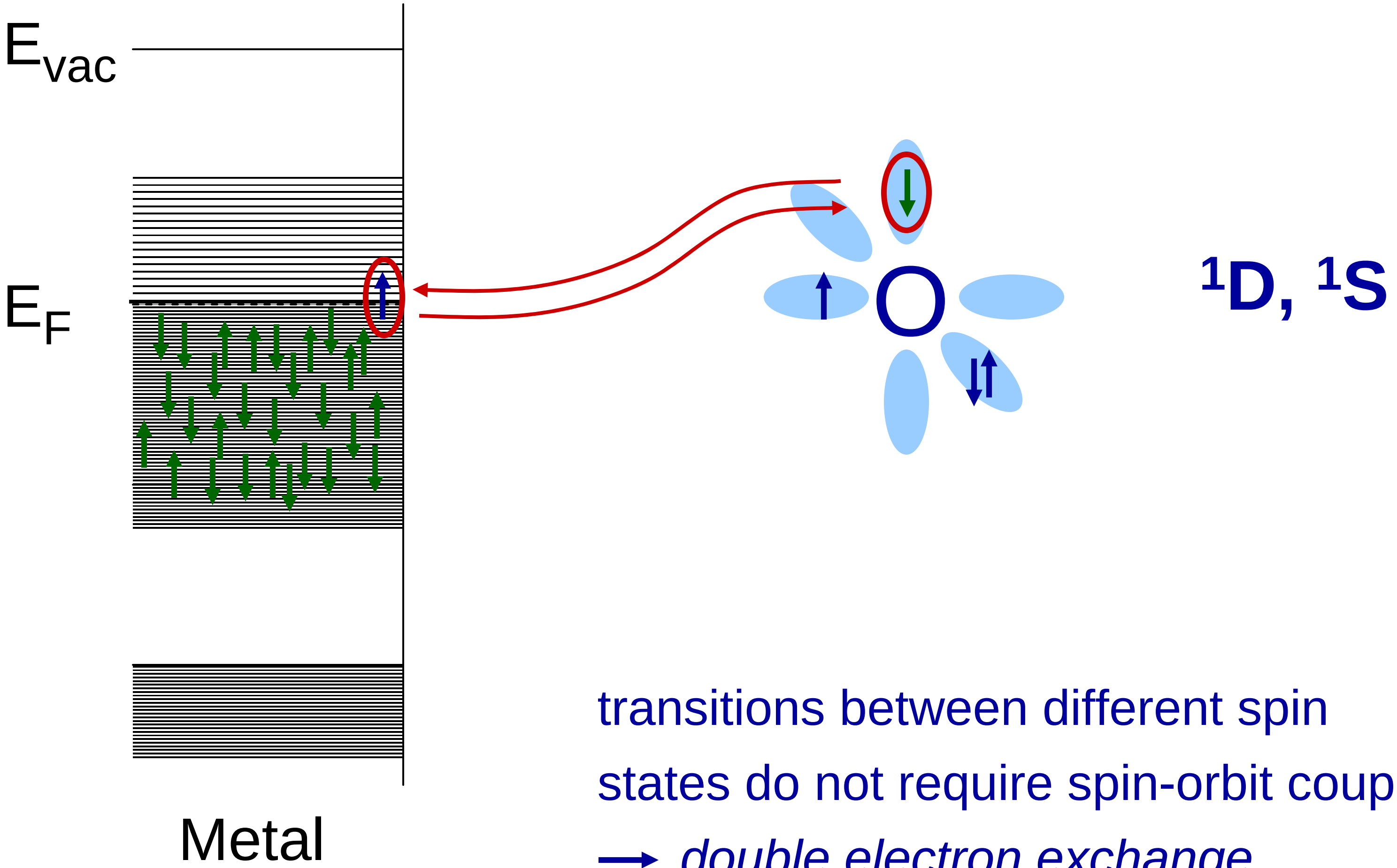
Gas-Surface



Electron energy levels in solids



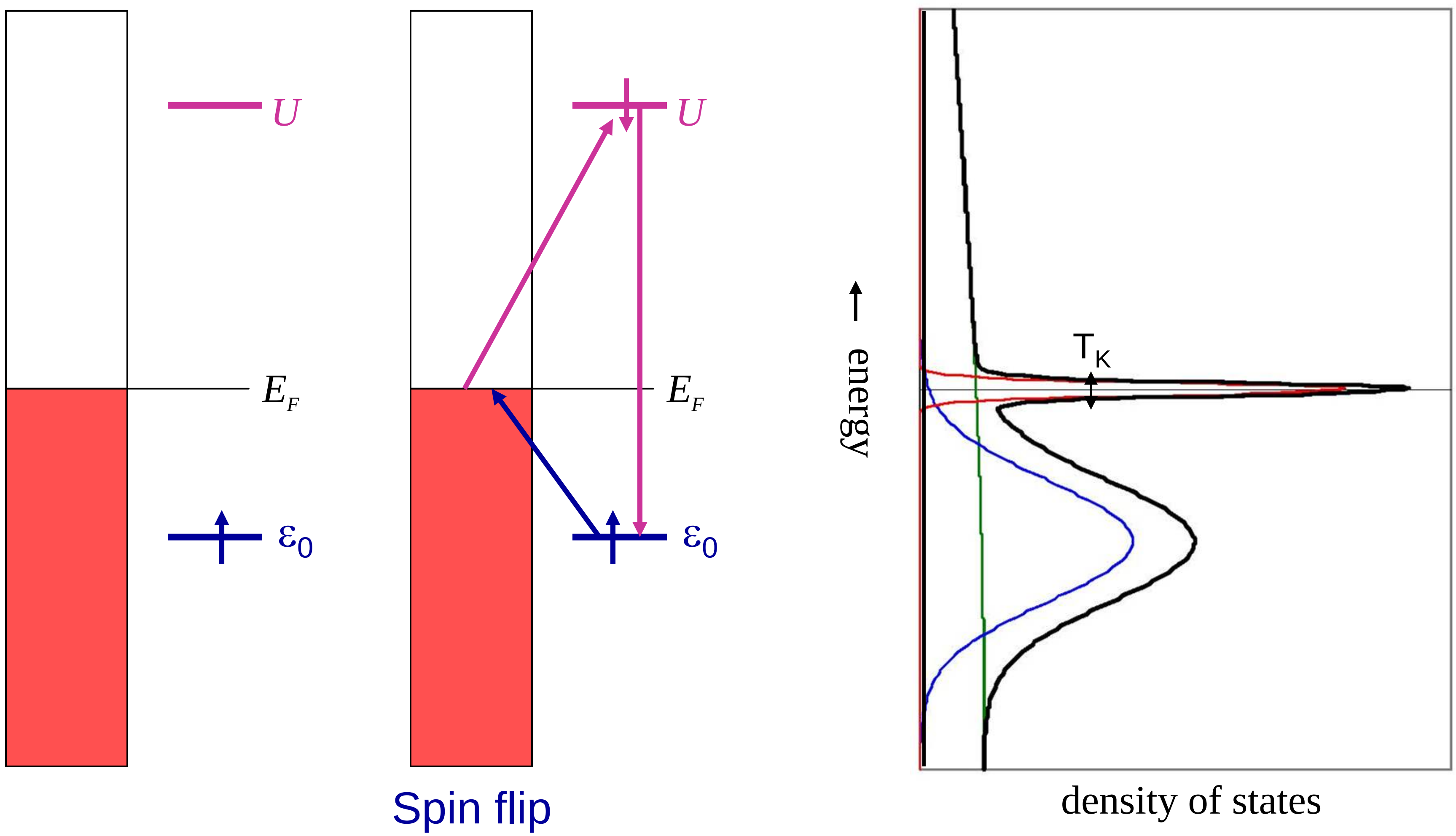

E_{vac}
E_F
Metal
O
^3P



transitions between different spin states do not require spin-orbit coupling:

→ *double electron exchange*

Kondo Effect:



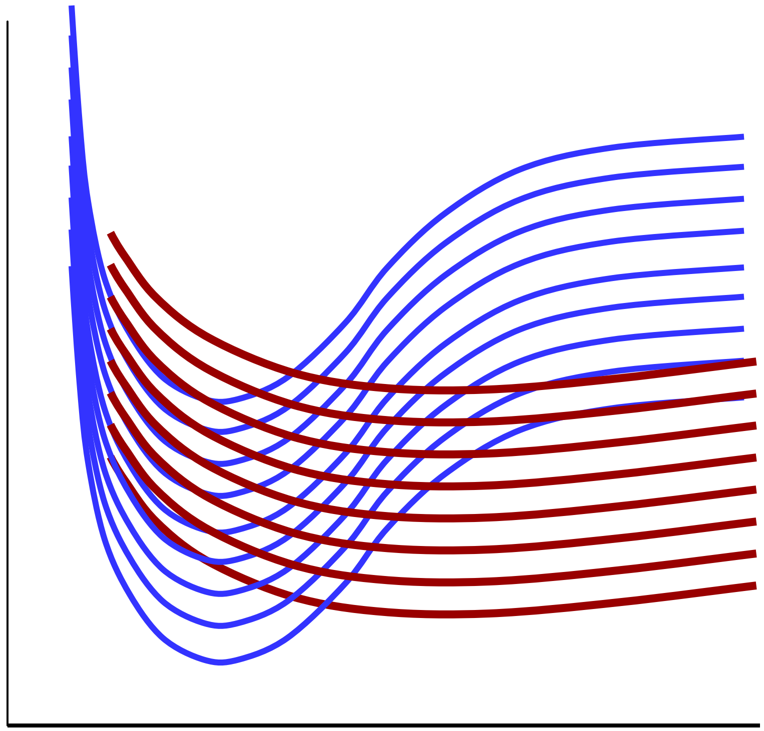
Dynamics at Metal Surfaces: <u>Challenges</u>

1. Compute excited state potential energy surfaces and off-diagonal (nonadiabatic) couplings

2. Simulate dynamics subject to multiple (myriads) of potential energy surfaces

Dynamics at Metal Surfaces: Challenges

1. Compute excited state potential energy surfaces
   and off-diagonal (nonadiabatic) couplings



need **diabatic** potential energy surfaces, widths, couplings

Dynamics at Metal Surfaces: <u>Challenges</u>

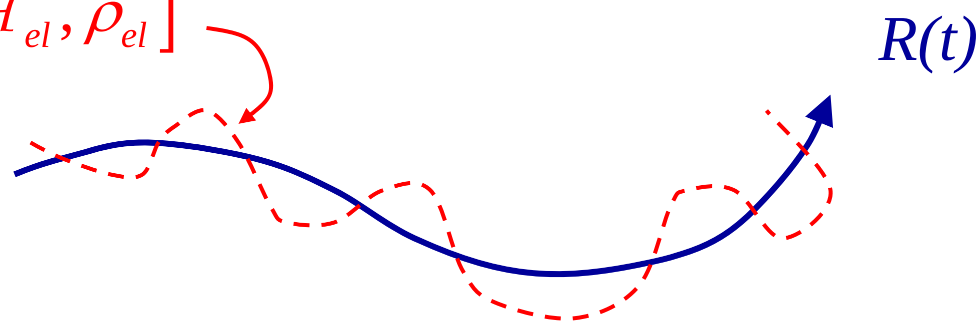
1. Compute excited state potential energy surfaces and off-diagonal (nonadiabatic) couplings

→ 2. Simulate dynamics subject to multiple (myriads) of potential energy surfaces

Mixed Quantum-Classical Dynamics

Mixed Quantum-Classical Dynamics

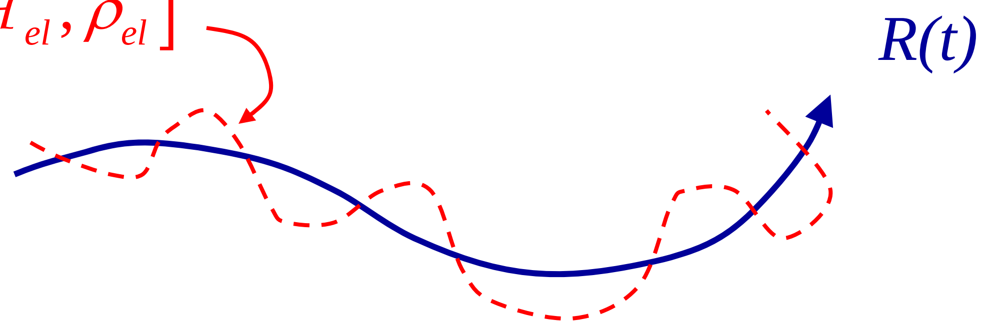
$$i\hbar \frac{\partial \rho_{el}}{\partial t} = \left[\mathcal{H}_{el}, \rho_{el} \right]$$



Propagate electronic density matrix along classical path

Mixed Quantum-Classical Dynamics

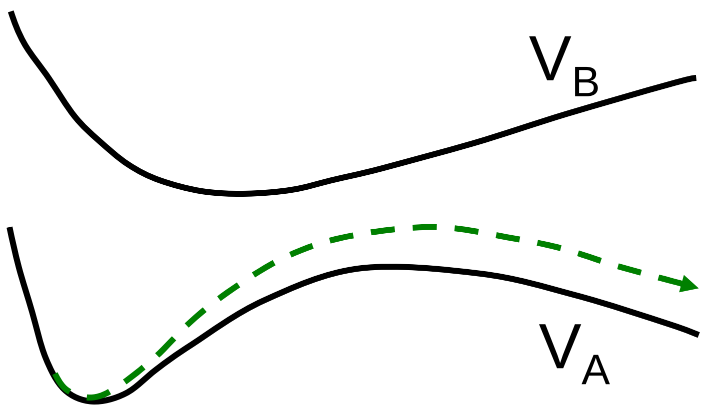
$$i\hbar \frac{\partial \rho_{el}}{\partial t} = \left[\mathcal{H}_{el}, \rho_{el} \right]$$

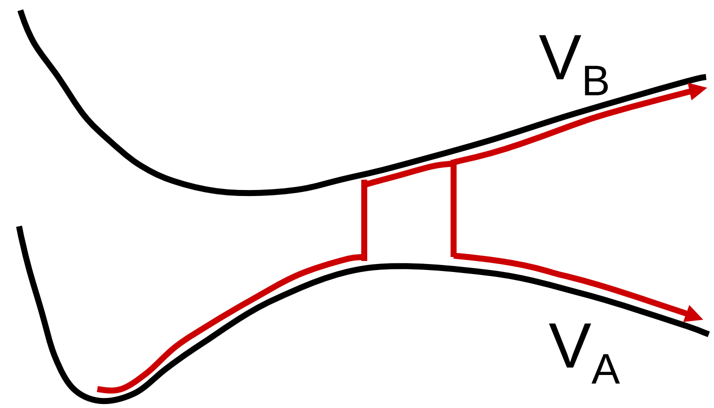


Classical path must respond **self-consistently** to quantum transitions: “quantum back-reaction”

The two main approaches – *Ehrenfest* and *Surface Hopping* - differ only in the treatment of back-reaction

MIXED QUANTUM-CLASSICAL STRATEGIES FOR INCLUDING QUANTUM BACK-REACTION





Ehrenfest

(self-consistent field)

weak ↓ coupling

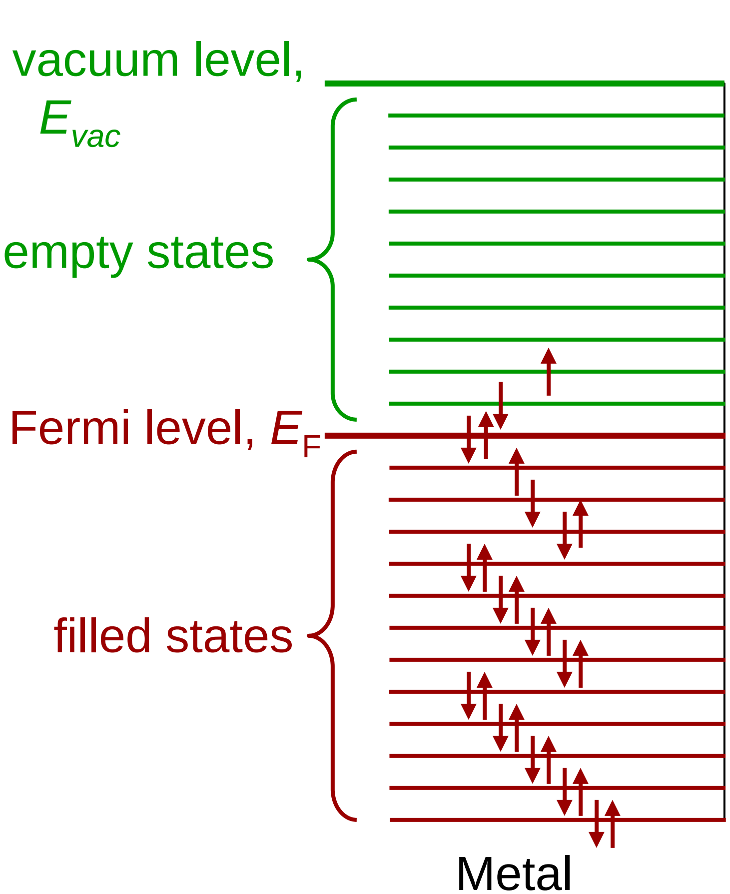
electronic friction

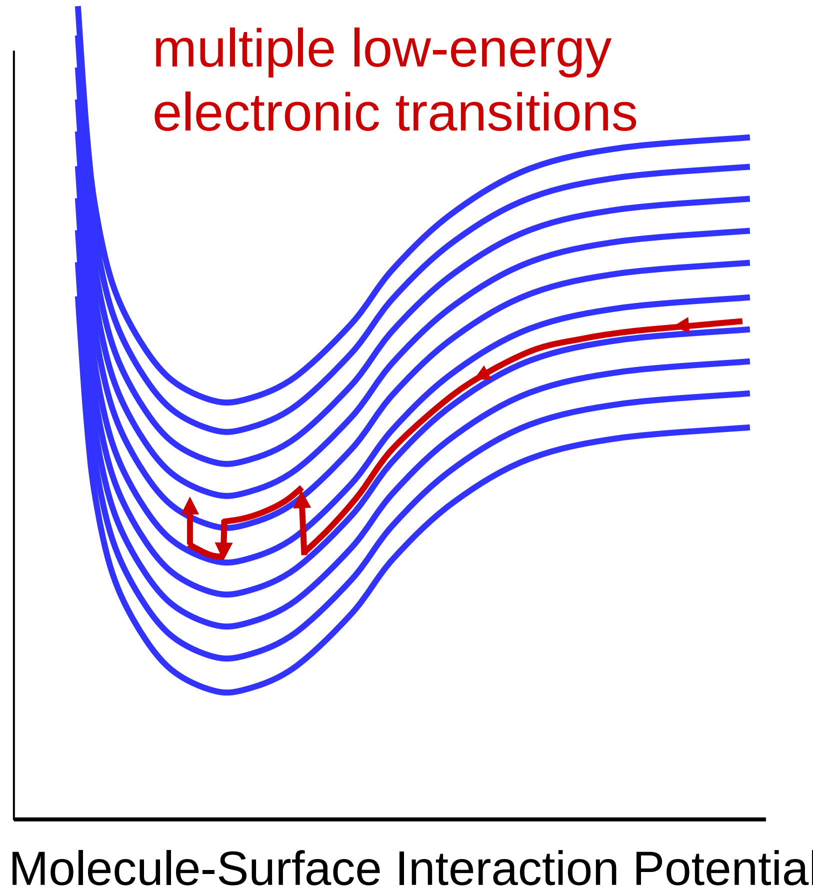
Surface-Hopping

(stochastic)

Electronic Friction: The effect of electron-hole pair transitions on dynamics at metal surfaces

M. Head-Gordon and JCT, *J. Chem. Phys*. **103**, 10137 (1995).
V. Krishna and JCT, *J. Chem. Phys.* **125**, 054706 (2006).

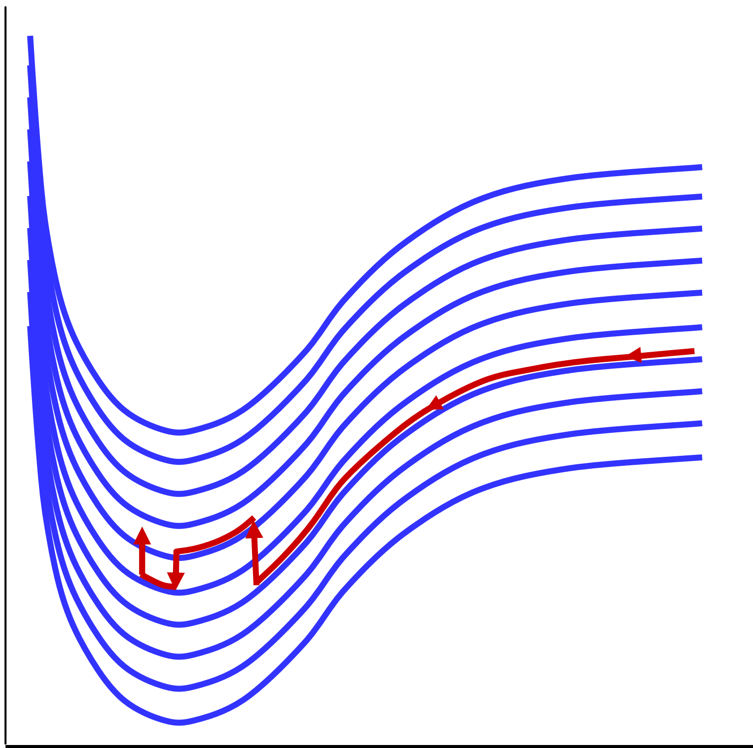


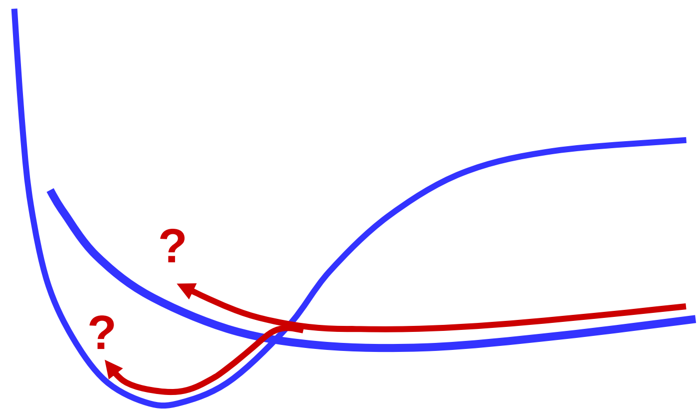


multiple low-energy
electronic transitions

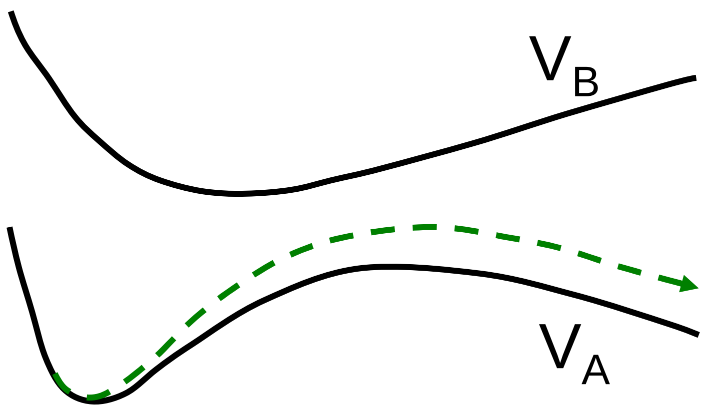
vs.

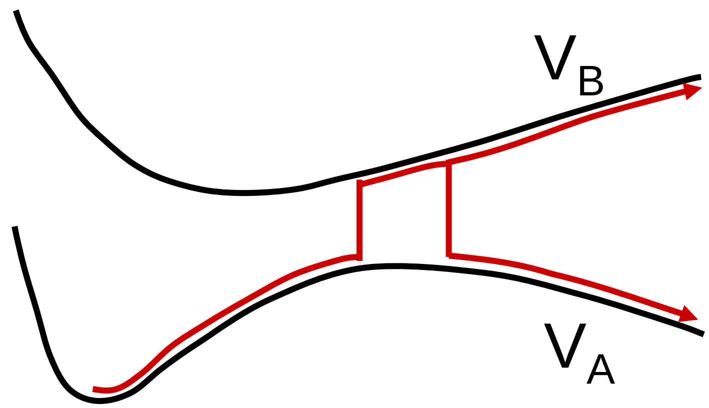
divergent pathways
on different potential
energy surfaces





MIXED QUANTUM-CLASSICAL STRATEGIES FOR INCLUDING QUANTUM BACK-REACTION





Ehrenfest

(self-consistent field)

weak ↓ coupling

electronic friction

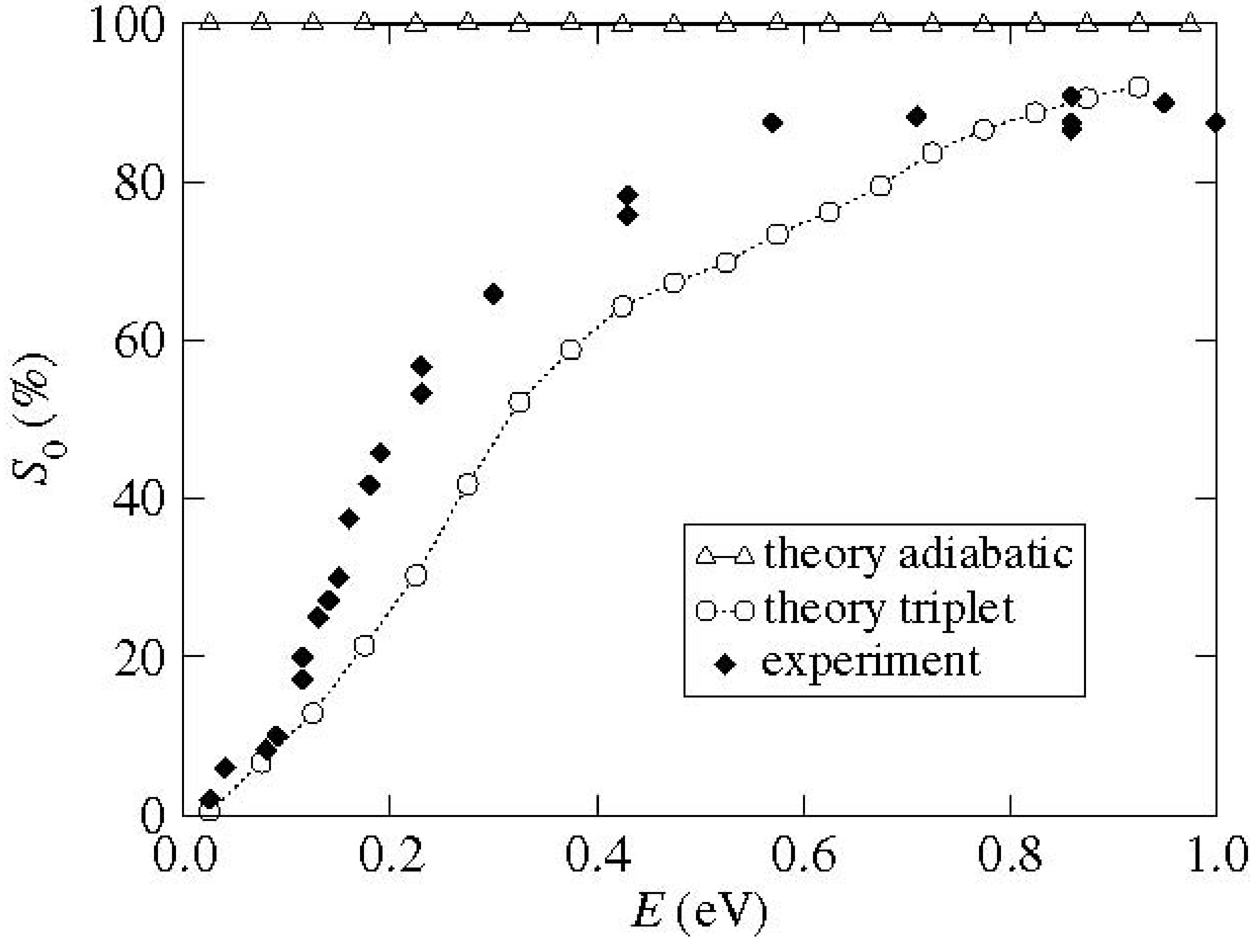
Surface-Hopping

(stochastic)

↓

motion on individual
potential energy surfaces

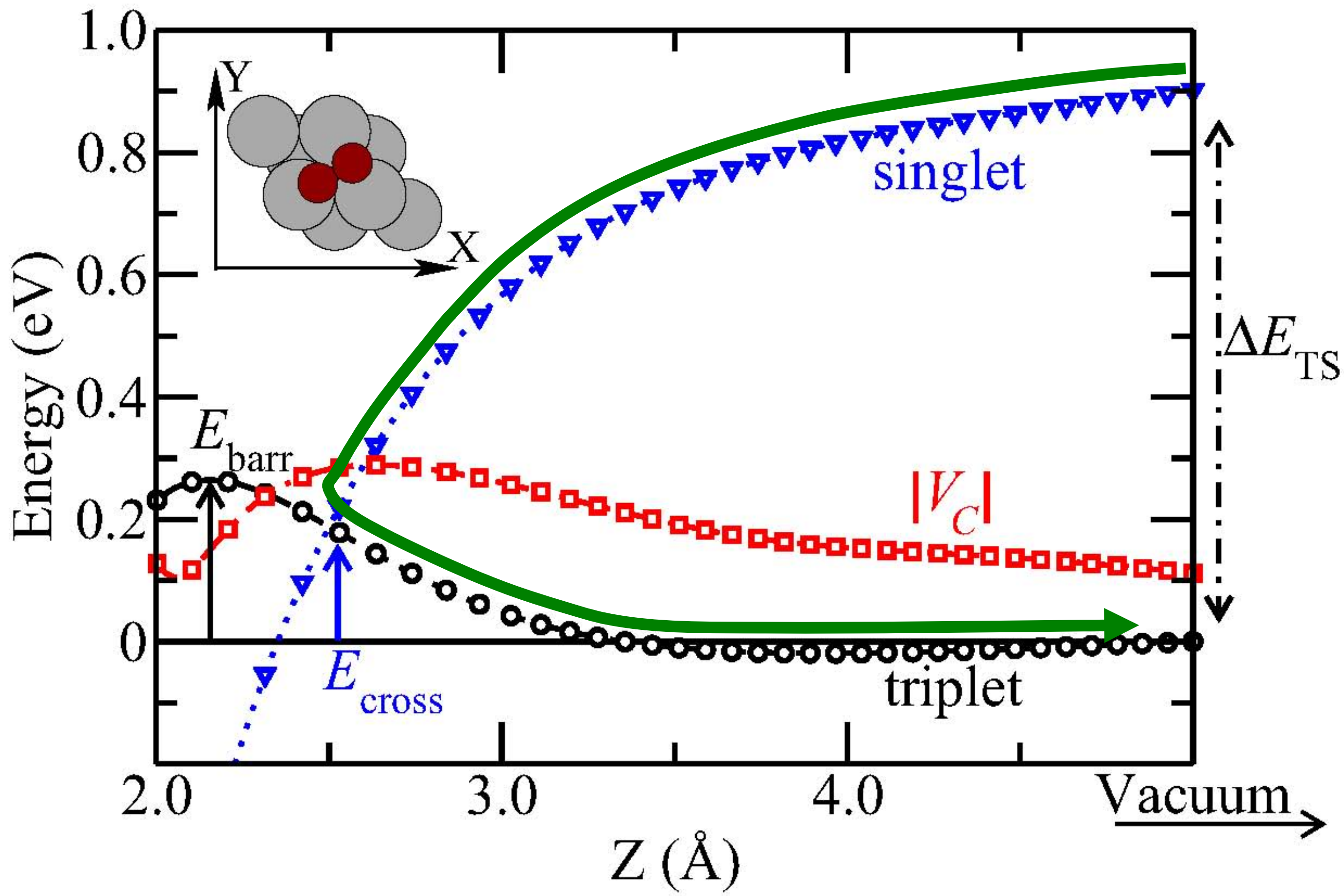
Dissociation of O_2 ($^3\Sigma$) on Al(111)



J. Behler, B. Delley, S. Lorenz, K. Reuter, and M. Scheffler, Phys. Rev. Lett. **94**, 2005

Fingerprints for spin-selection rules in the interaction dynamics of O_2 at Al(111),

C. Carbogno, J. Behler, A. Groß, and K. Reuter, *Phys. Rev. Lett*., **101**, 096104 (2008)



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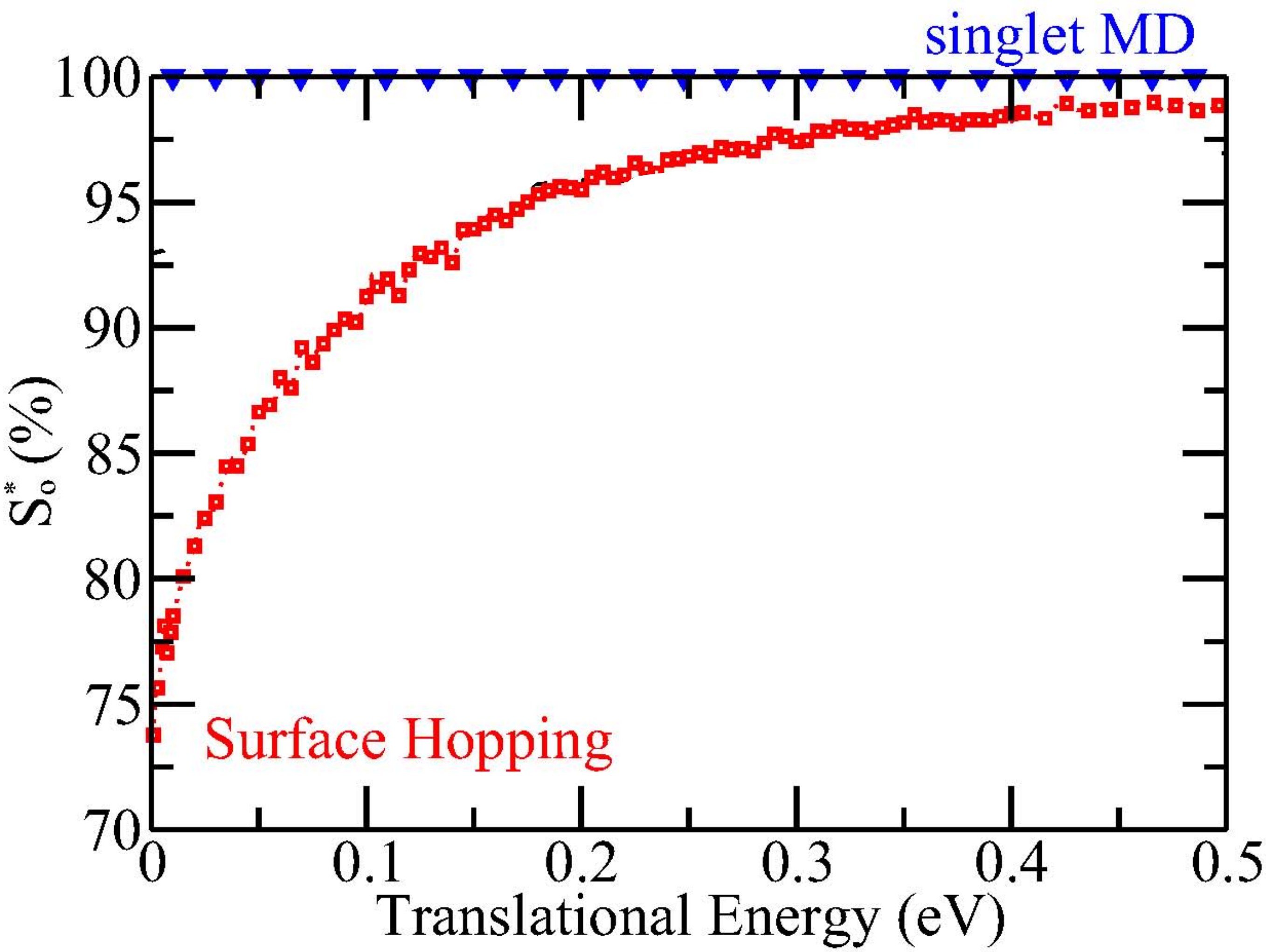
C. Carbogno, J. Behler, A. Groß, and K. Reuter, *Phys. Rev. Lett.*, **101**, 096104 (2008)



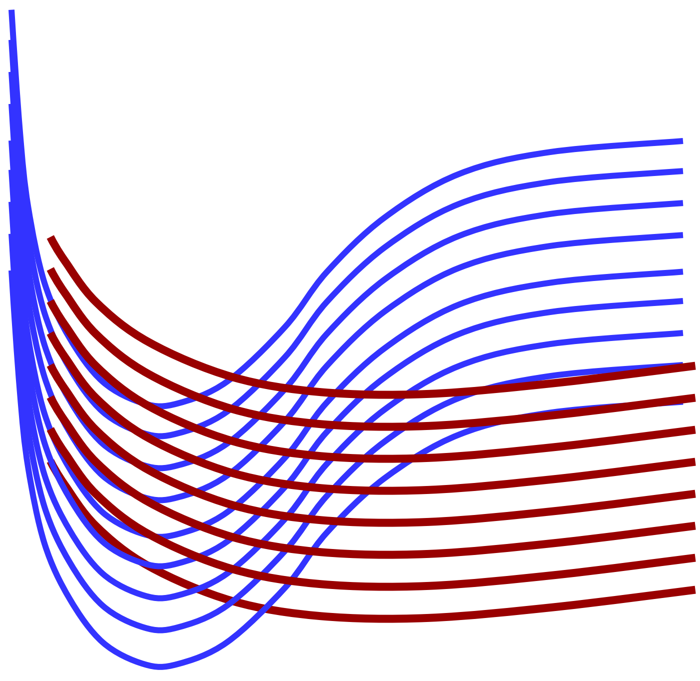
Dynamics at Metal Surfaces: <u>Challenges</u>

1. Compute excited state potential energy surfaces and off-diagonal (nonadiabatic) couplings

2. Simulate dynamics subject to multiple (myriads) of potential energy surfaces

How to include continuum of electronic states?

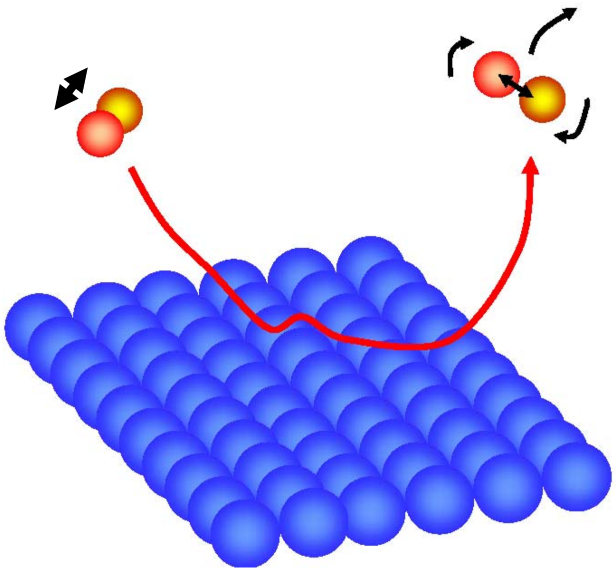
i.e., treat multiple states and e-h pair friction on an equal footing?

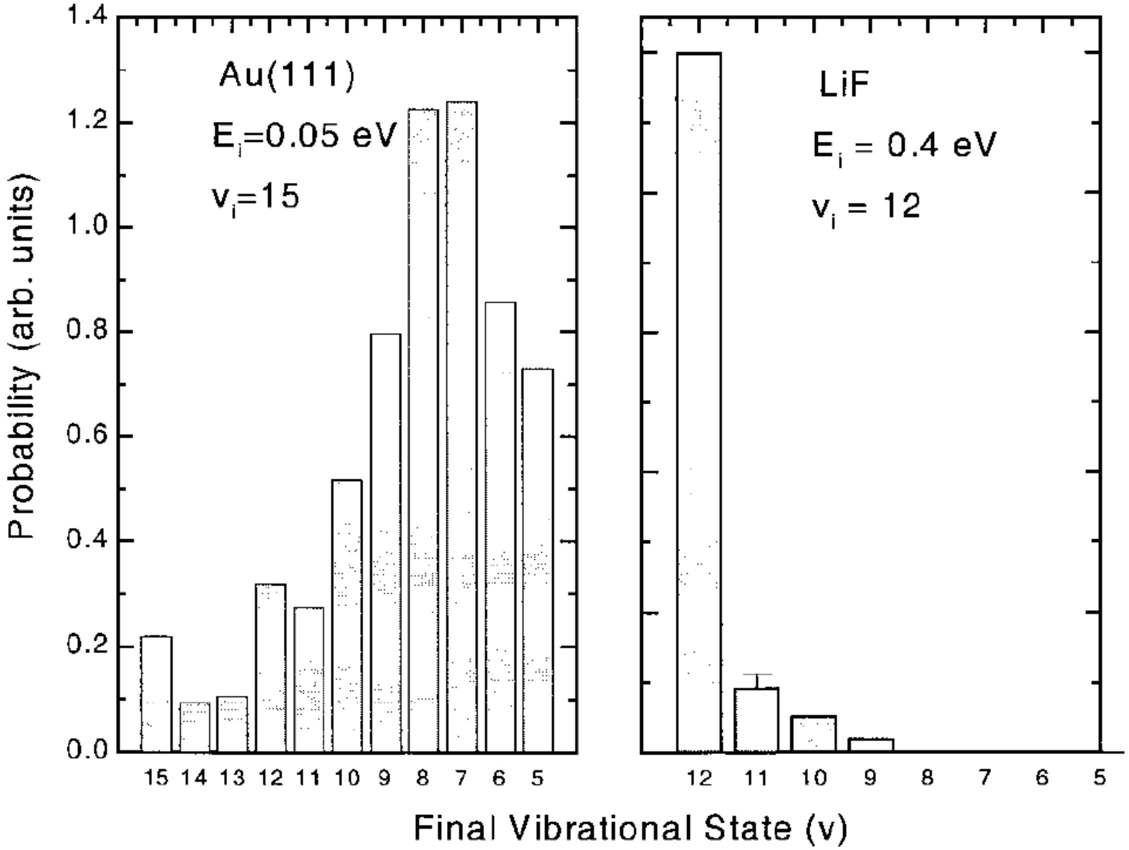


Test Case:

Scattering of vibrationally excited NO from Au(111)

Experiments of Alec Wodtke and coworkers, UCSB

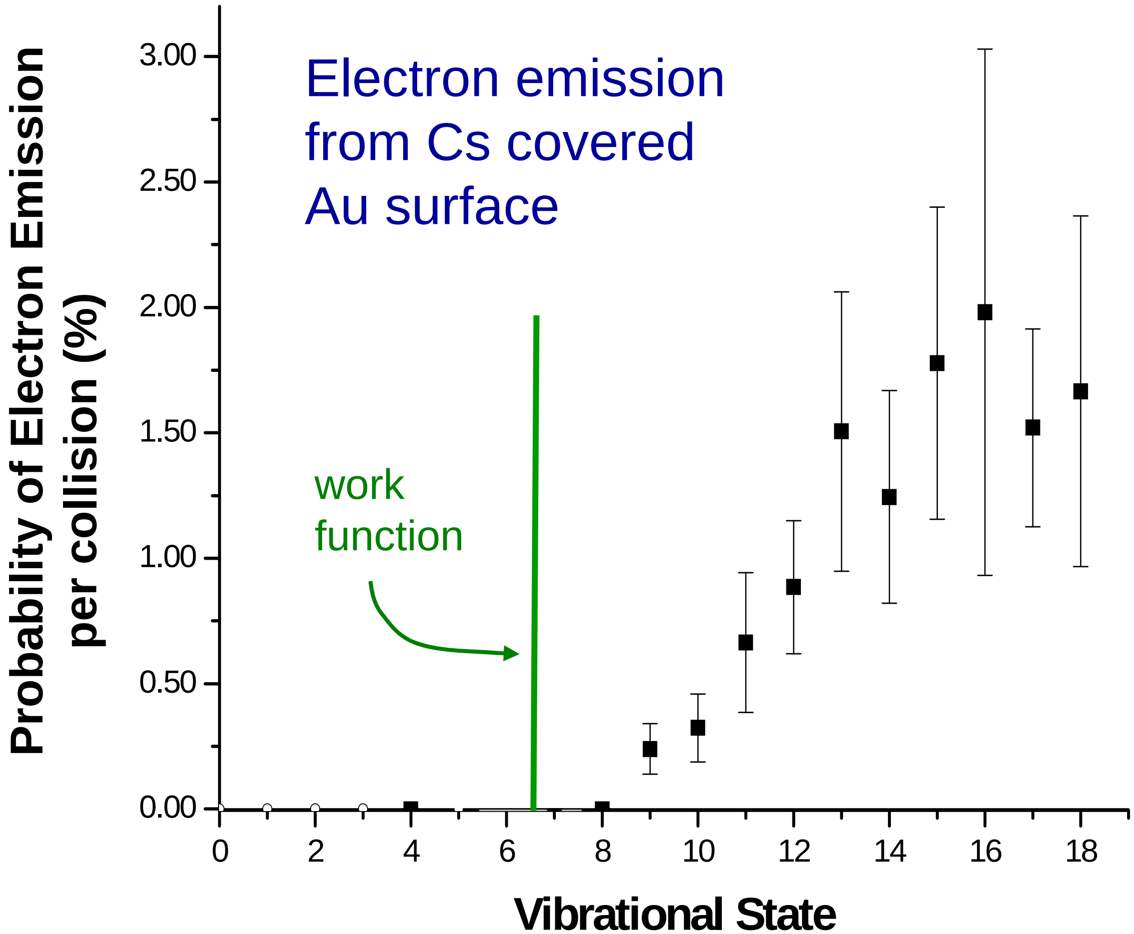




Huang, Rettner, Auerbach, Wodtke, *Science* **2000**, *290*, 111.

Electron Emission:

→ *inadequacy of electronic friction model ?*

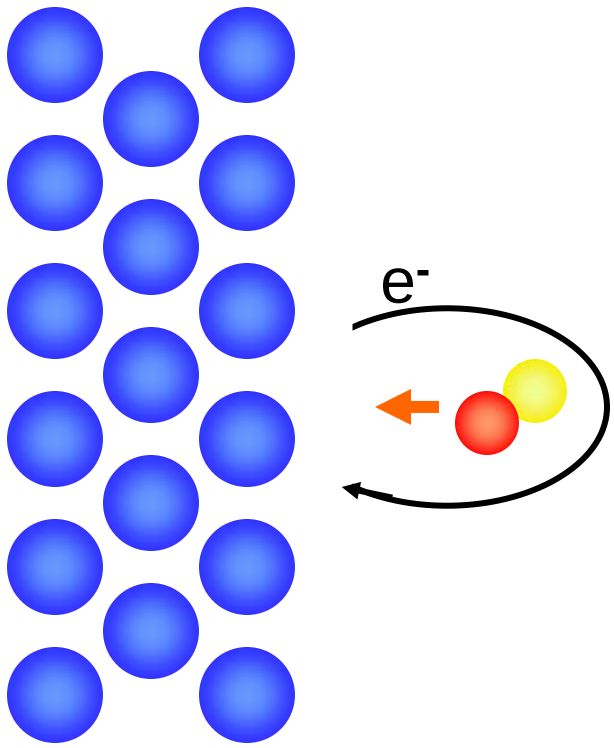


White, J. D.; Chen, J.; Auerbach, D. J.; Wodtke, A. M. *Nature* **2005**, *433*, 503.

Electronic excitations at metal surfaces?

Inelastic Electron Scattering Picture:

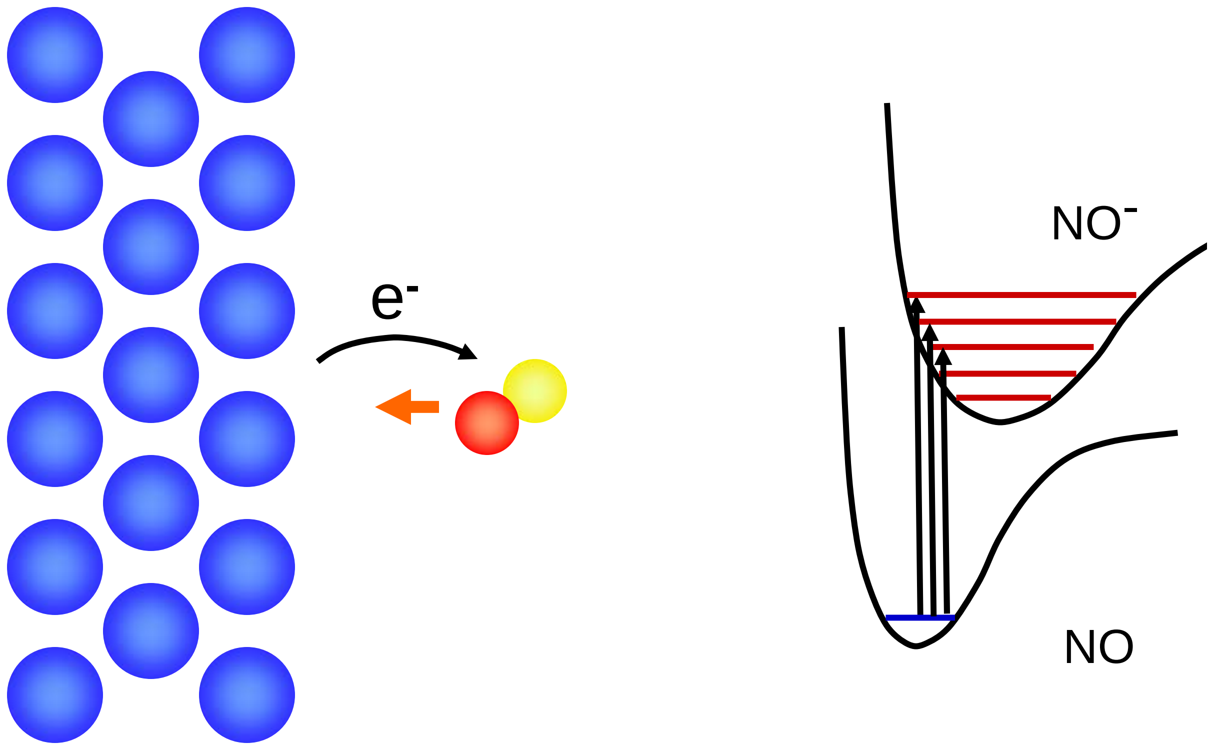
a. Non-Resonant → *friction model*



Electronic excitations at metal surfaces?

Alternative Franck-Condon Mechanism:

b. Resonant → *transient negative ion*



Electronic excitations at metal surfaces?

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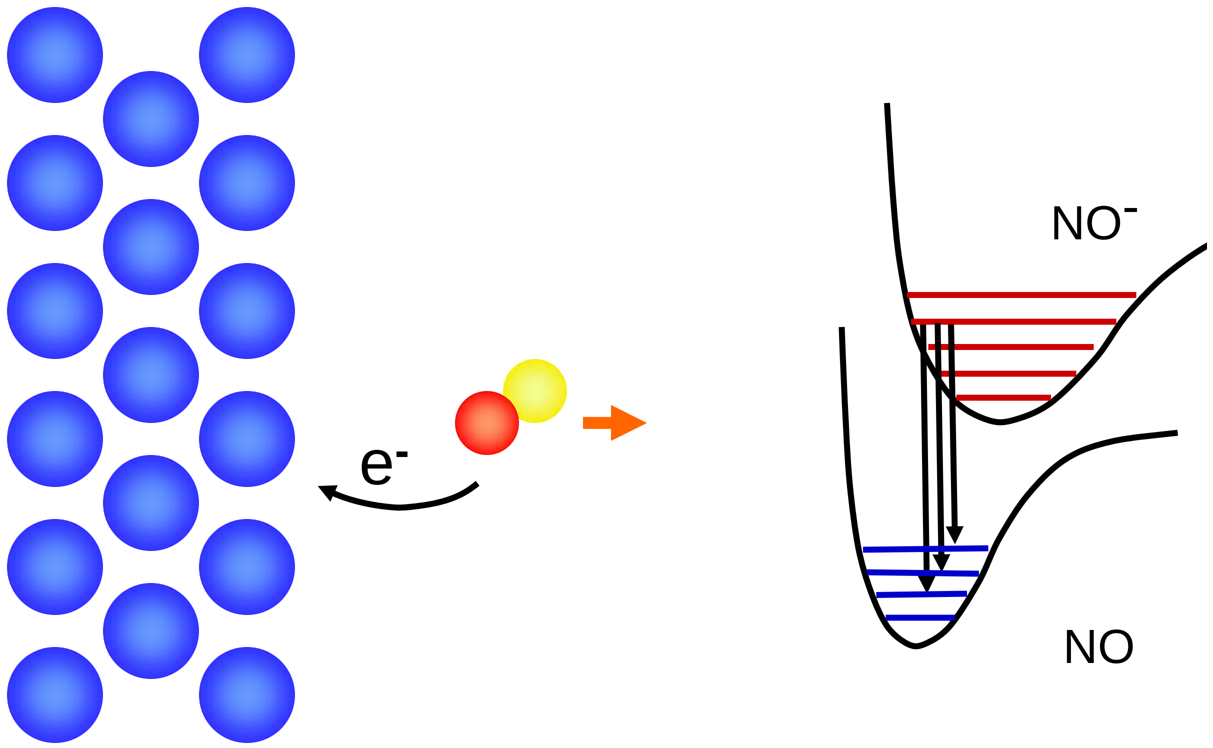

Electronic excitations at metal surfaces?

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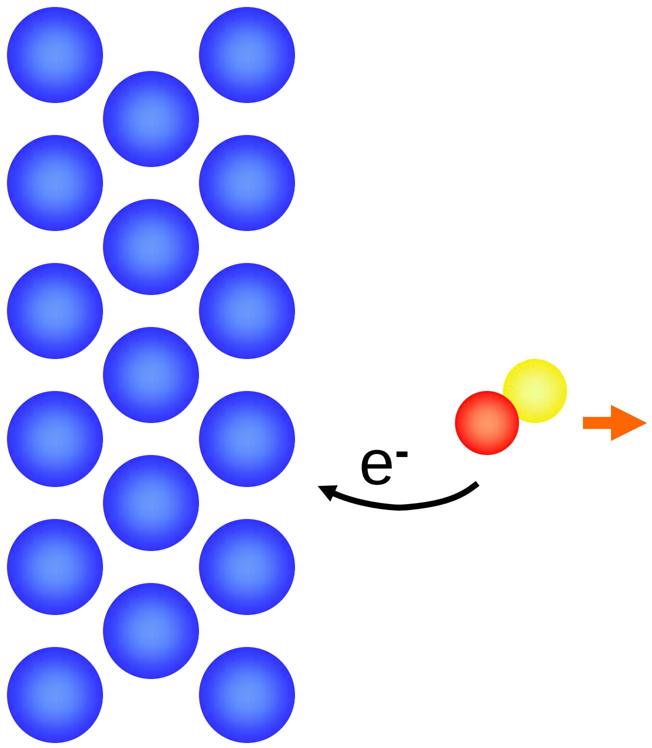
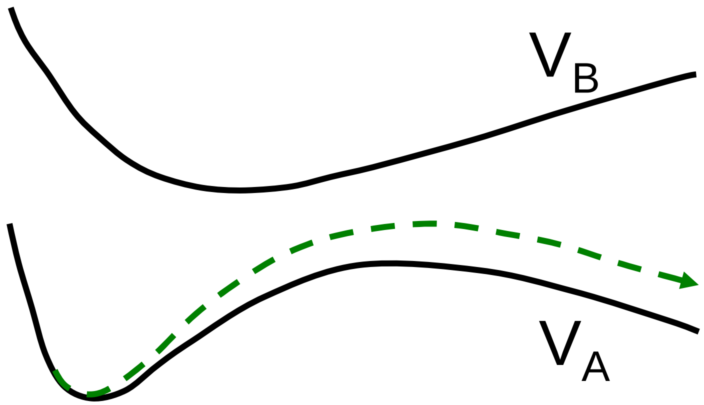


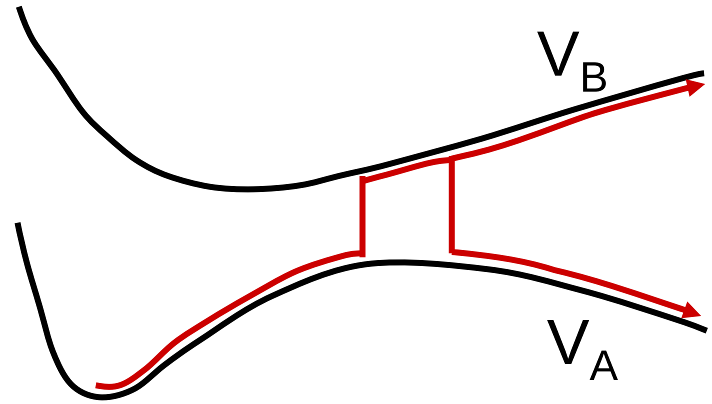
See:

J. W. Gadzuk

Can we unify friction and resonance models?

MIXED QUANTUM-CLASSICAL STRATEGIES FOR INCLUDING QUANTUM BACK-REACTION





Ehrenfest

(self-consistent field)

weak ↓ coupling

electronic friction

Surface-Hopping

(stochastic)

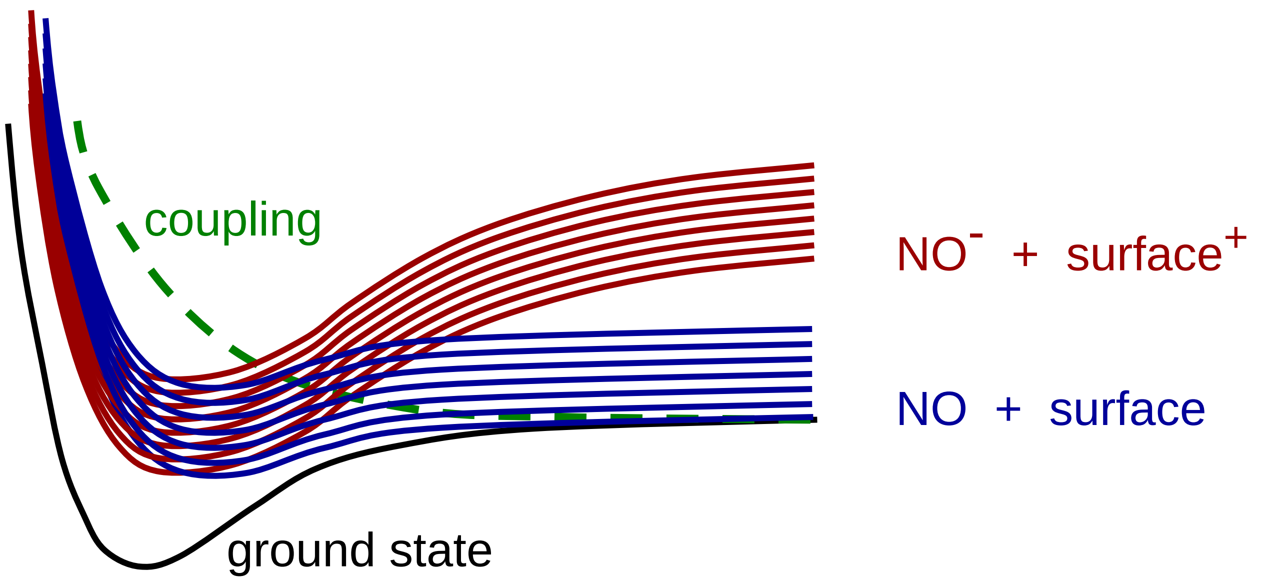
↓

motion on individual
potential energy surfaces

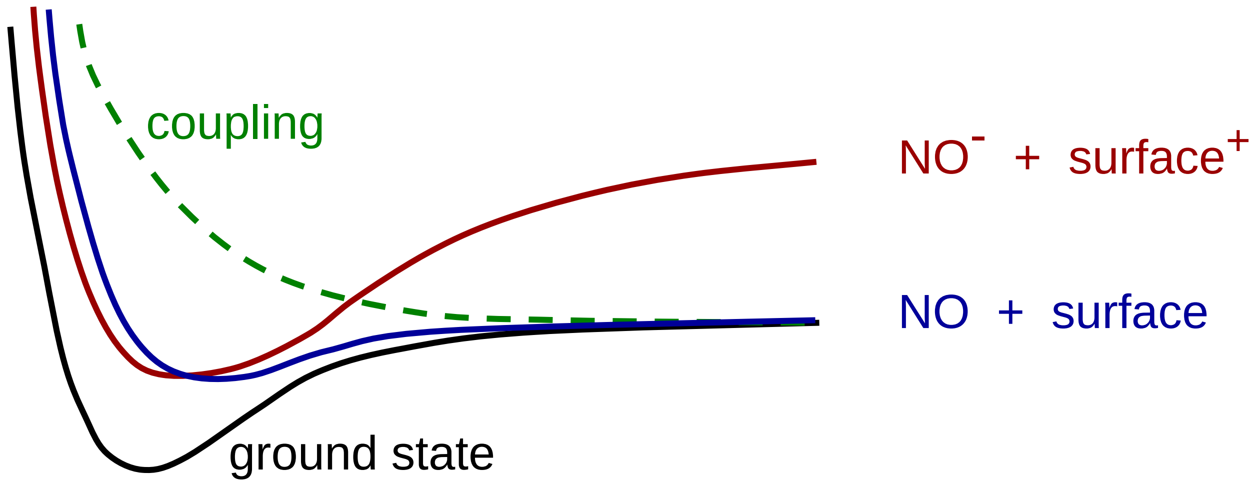
How do we do surface hopping among **huge** numbers of potential energy surfaces?

1. How do we compute **adiabatic** potential energy surfaces and nonadiabatic couplings? *Newns-Anderson Hamiltonian*

2. How do we integrate surface hopping trajectories? *Independent Electron Surface Hopping*



Nitric Oxide on Gold: Diabatic Description

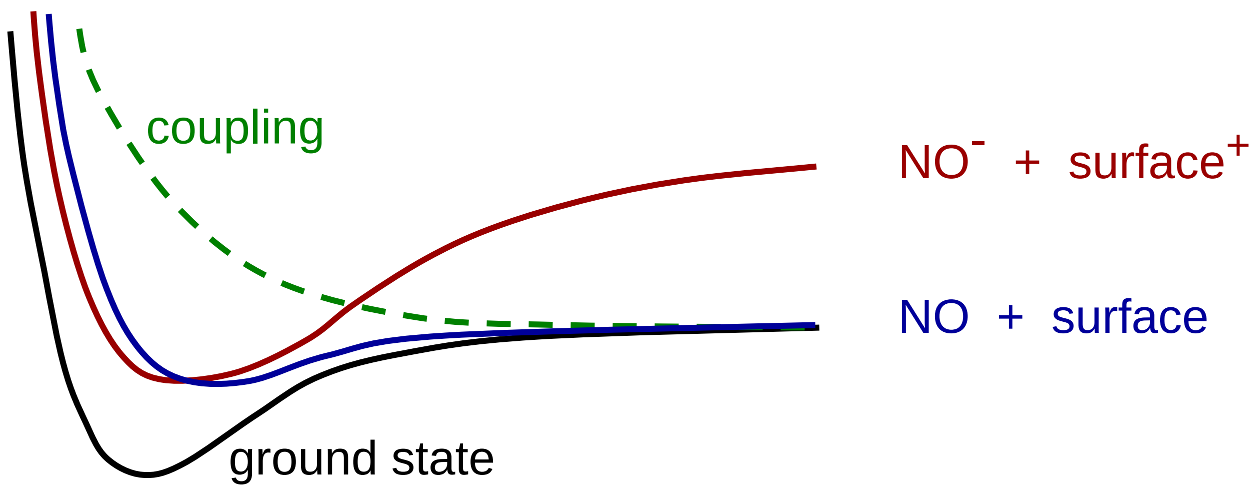


initially pretend there is no continuum:

carry out ground state DFT calculations for large number of N, O, and Au atomic positions (VASP, PW91)

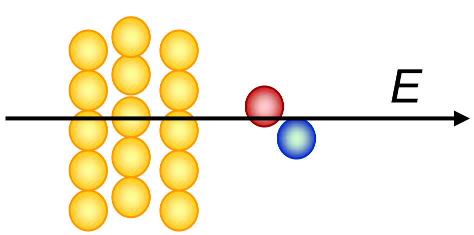
But see Patrick Rinke talk: "CO Adsorption Puzzle"

Nitric Oxide on Gold: Diabatic Description



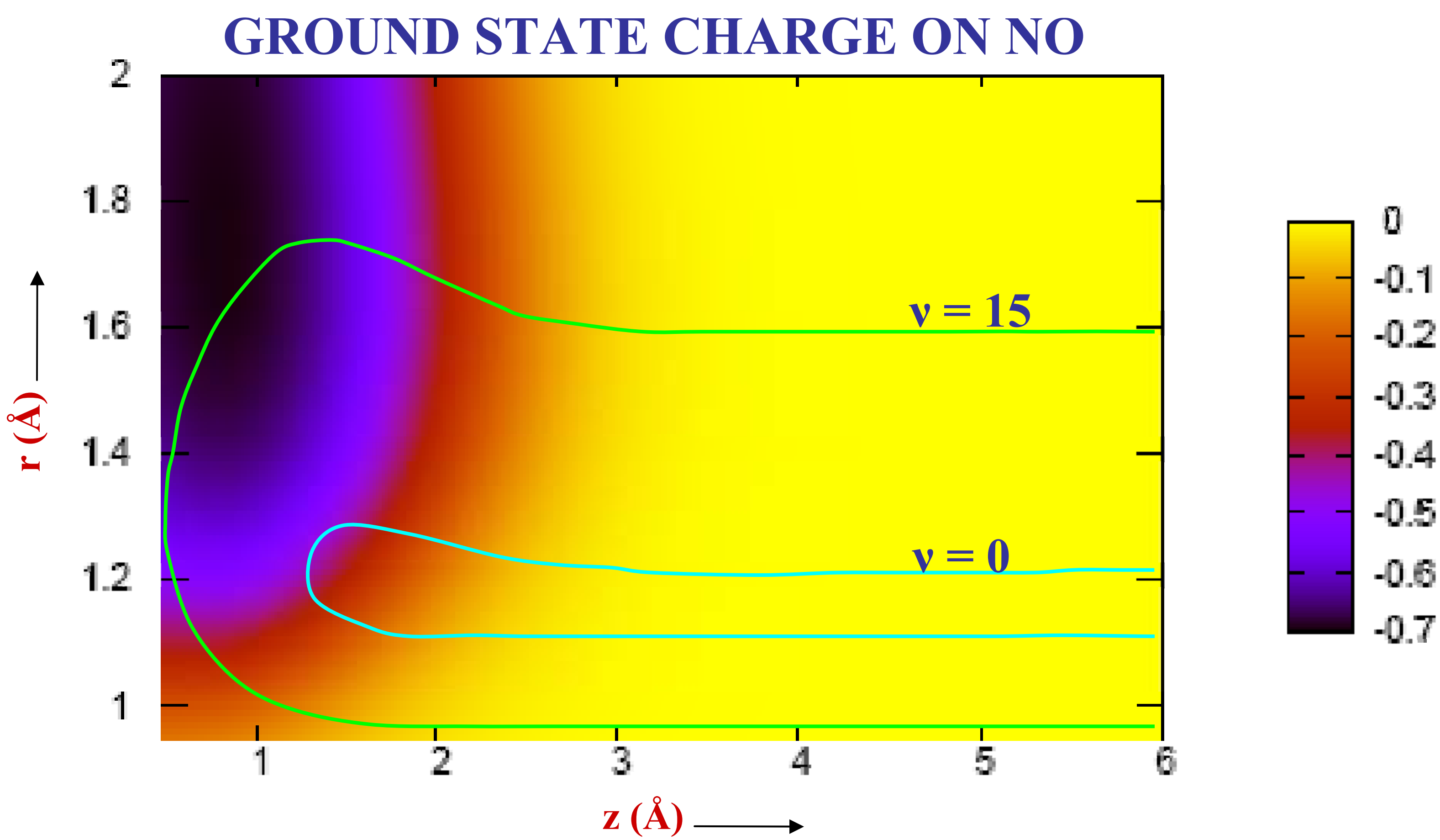
$$\begin{bmatrix} E_{ionic}(\mathbf{R}) & V(\mathbf{R}) \\ V(\mathbf{R}) & E_{neutral}(\mathbf{R}) \end{bmatrix}$$ → 3 unknowns

DFT calculation → ground state energy
effective charge on NO



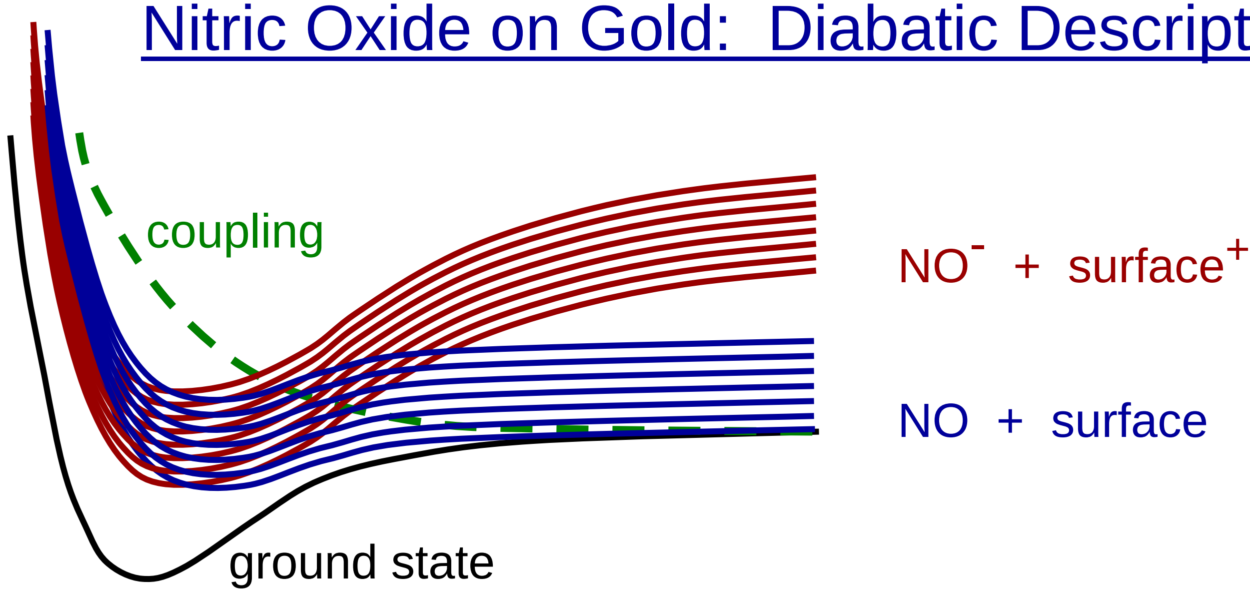
add small electric field → 3^d quantity

NO approaching a three-fold site on Au(111)



NO significantly charged when close to Au(111) and stretched to long bond lengths

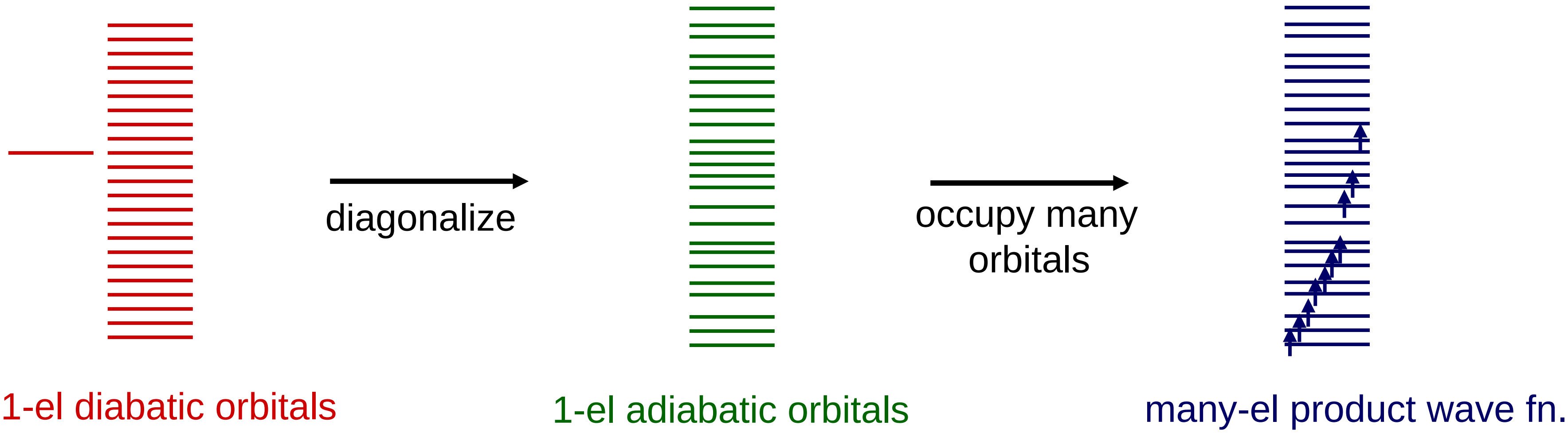
Nitric Oxide on Gold: Diabatic Description



Map onto Newns-Anderson Hamiltonian

1. Density of states is uniform
2. Coupling to localized state is uniform
3. Approx continuum with 40 levels

1. Map onto Anderson-Newns picture:



2. Evolve many-electron wave function along trajectory:

initial many -electron wave fn (eg, ground state) → each orbital evolves into linear comb of diabatic (or adiabatic) orbitals → many-el wave fn at any time is a specific occupation of these evolving mixed orbitals

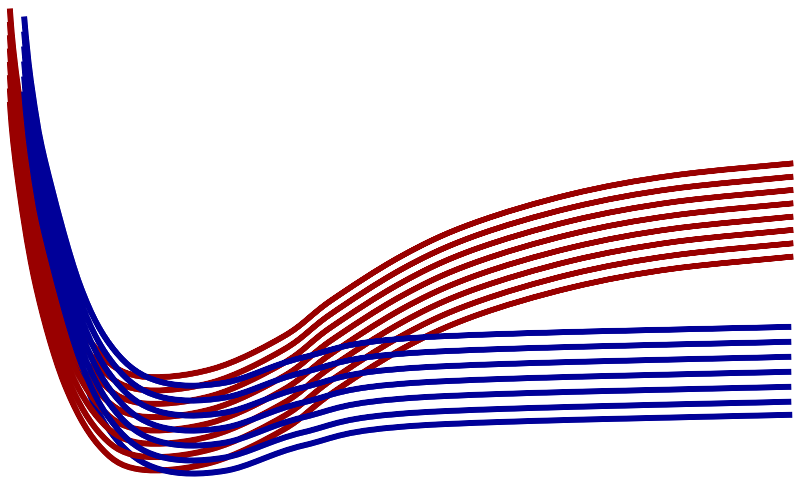
3. Surface Hop among adiabatic potential energy surfaces

SIMULATIONS: NO on Au(111)

1. Adiabatic

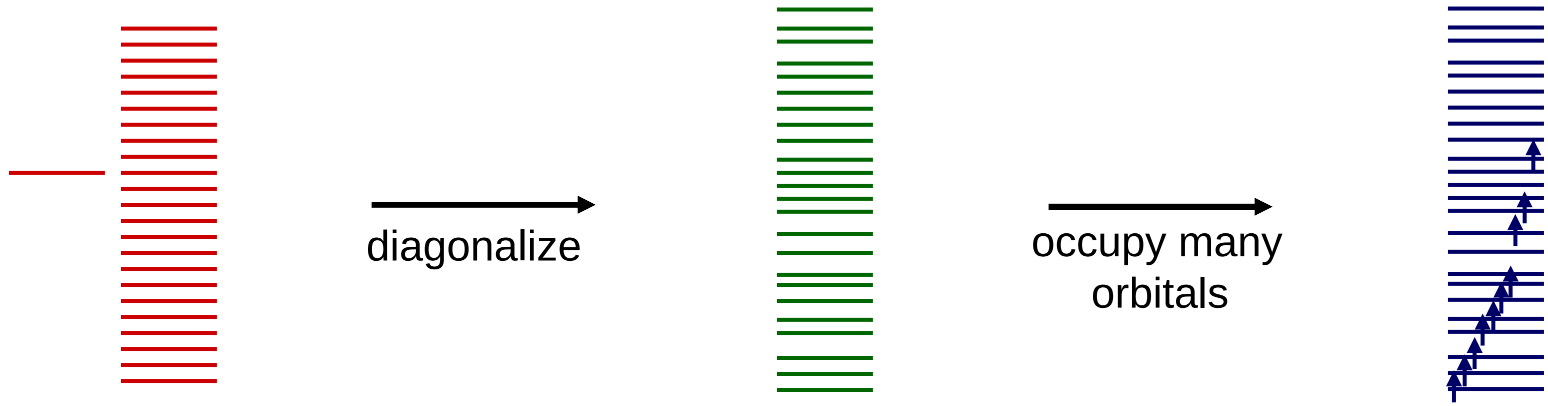
2. Nonadiabatic: Electronic Friction

3. Nonadiabatic: Surface Hopping among myriads of ***adiabatic*** potential energy surfaces



Key: independent electron hops

1. Map onto Anderson-Newns picture:



1-el diabatic orbitals | 1-el adiabatic orbitals | many-el product wave fn.

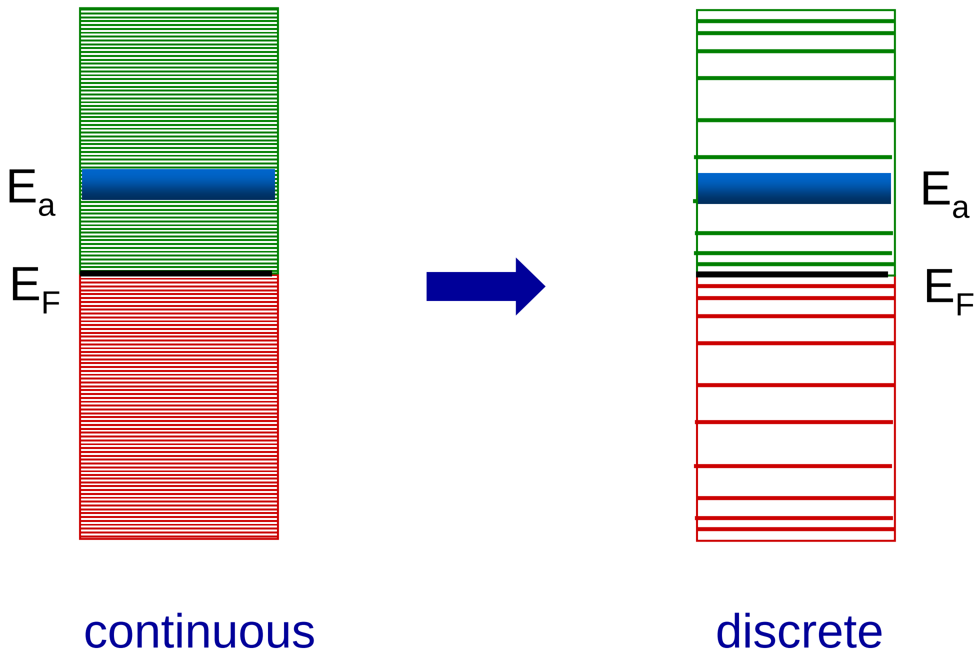
1 + 40 | **41** | **20 electrons → ~ 10^{11} states**

2. Evolve many-electron wave function along trajectory:

initial many -electron wave fn (eg, ground state) → each orbital evolves into linear comb of diabatic (or adiabatic) orbitals → many-el wave fn at any time is a specific occupation of these evolving mixed orbitals

3. Surface Hop among adiabatic potential energy surfaces

Discretization of the Continuum:

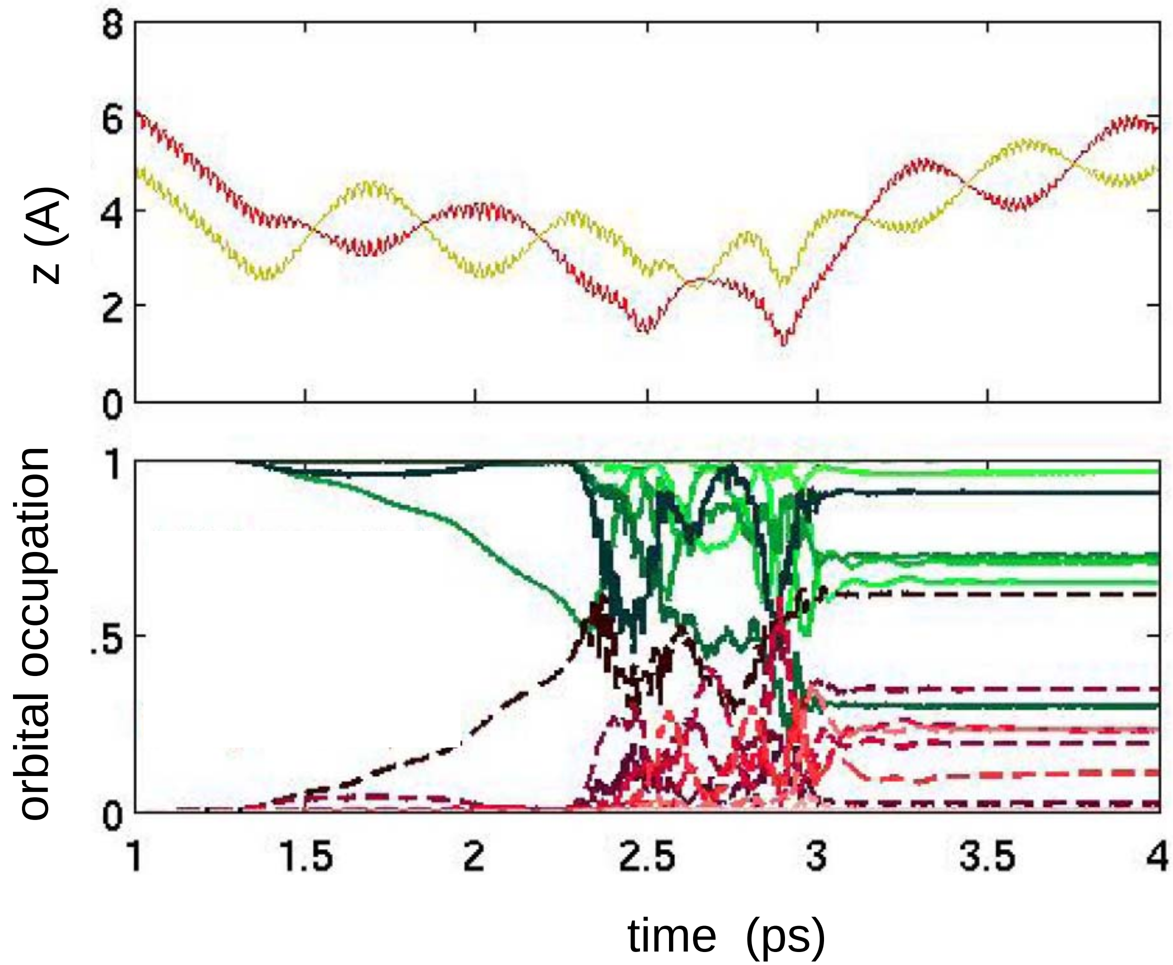


Optimally (non-equally) spaced discrete levels

"Efficient discretization of the continuum through contour integration",
N. Shenvi, J. R. Schmidt, S. Edwards and JCT, *Phys. Rev*. A **78**, 022502 (2008)

NO(v=15) scattered from Au(111) (*surface hopping trajectory*)

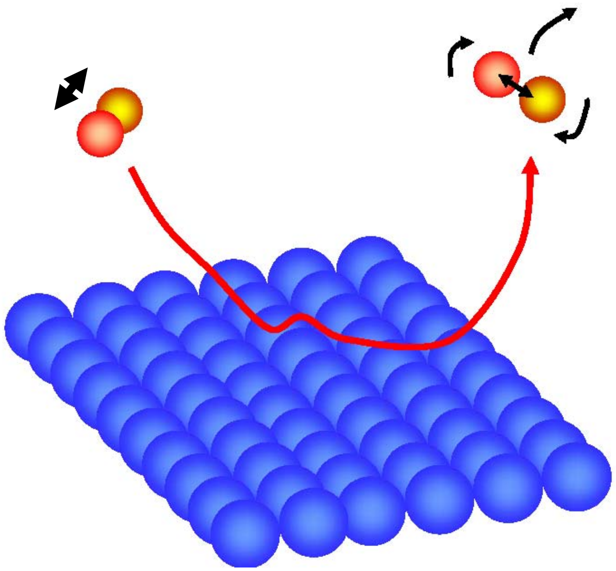
132 moving Au atoms, accurate phonon spectrum, periodic boundaries, etc.

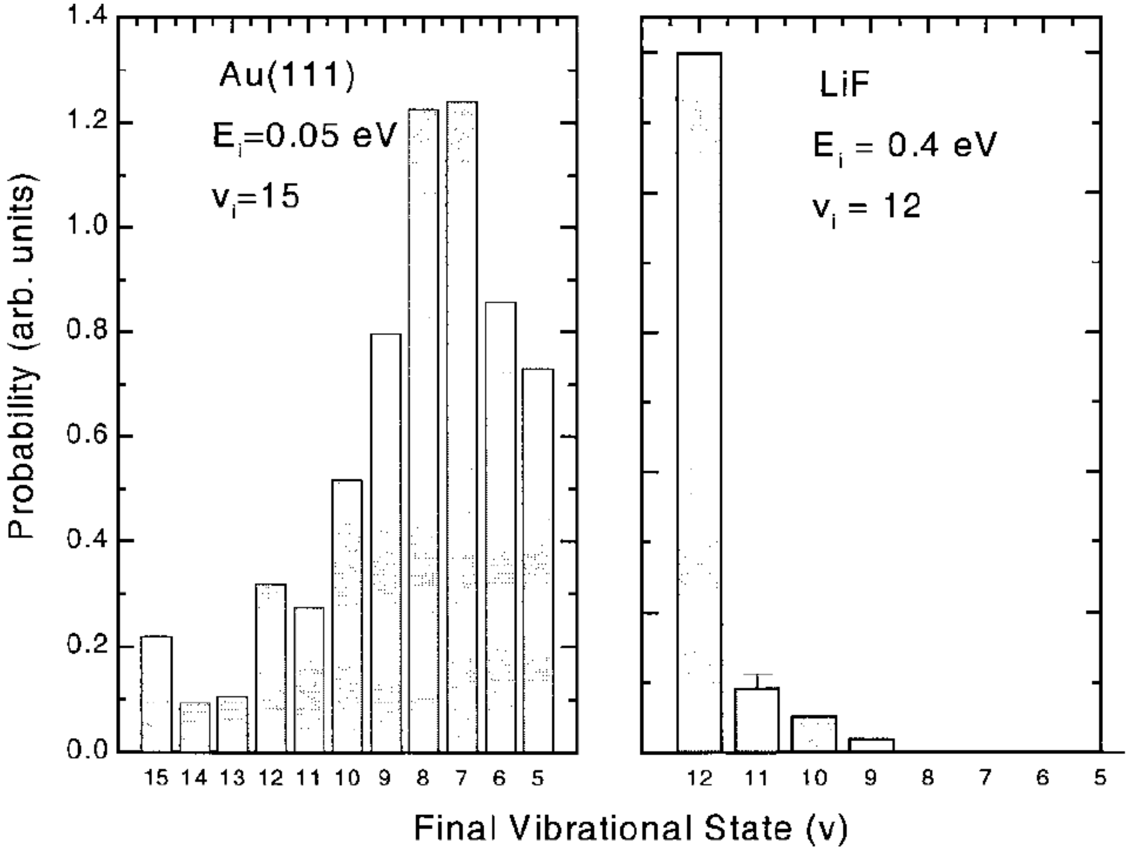


~ 100 surface hops typically encountered

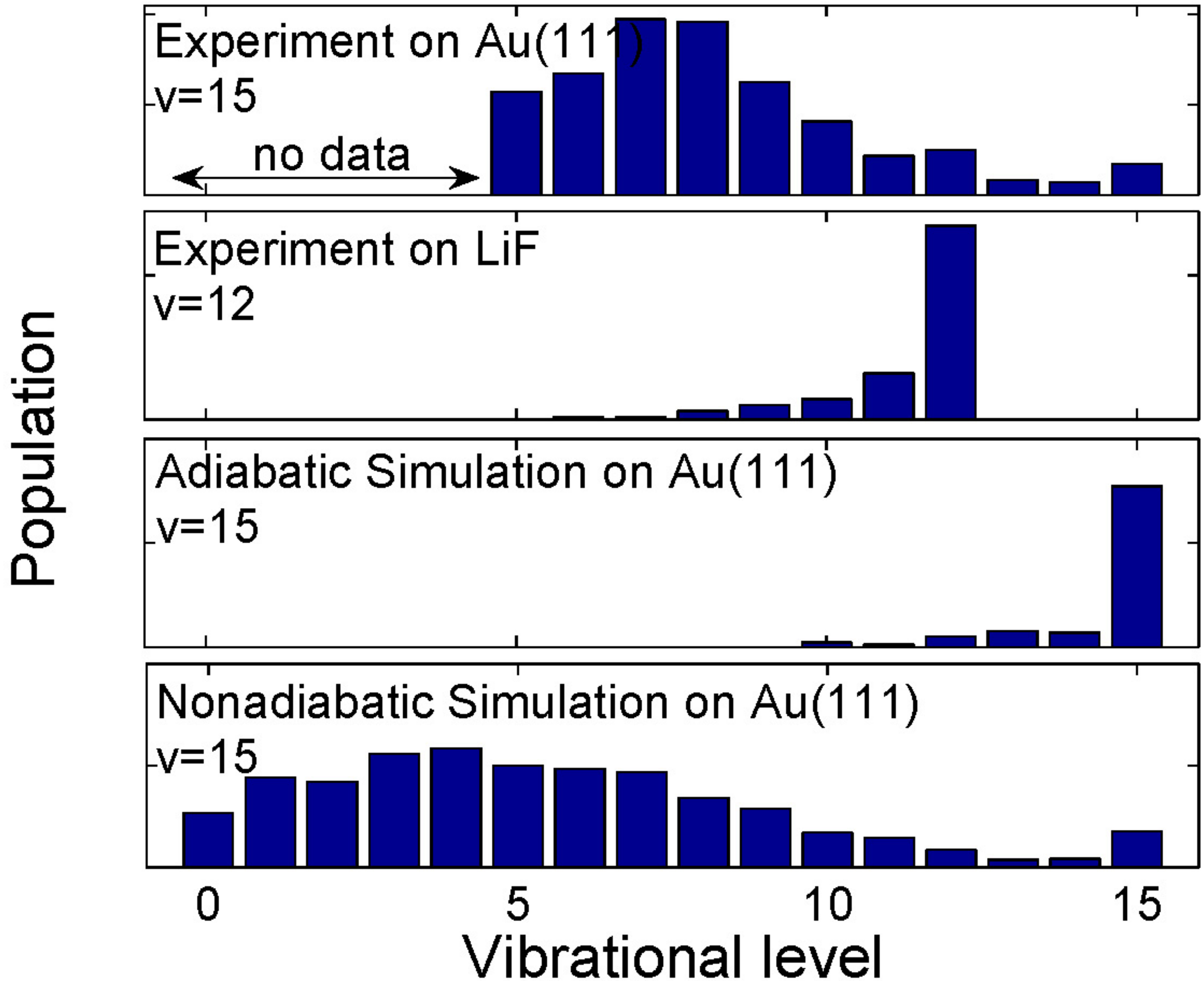
Scattering of vibrationally excited NO from Au(111)

Experiments of Alec Wodtke and coworkers, UCSB



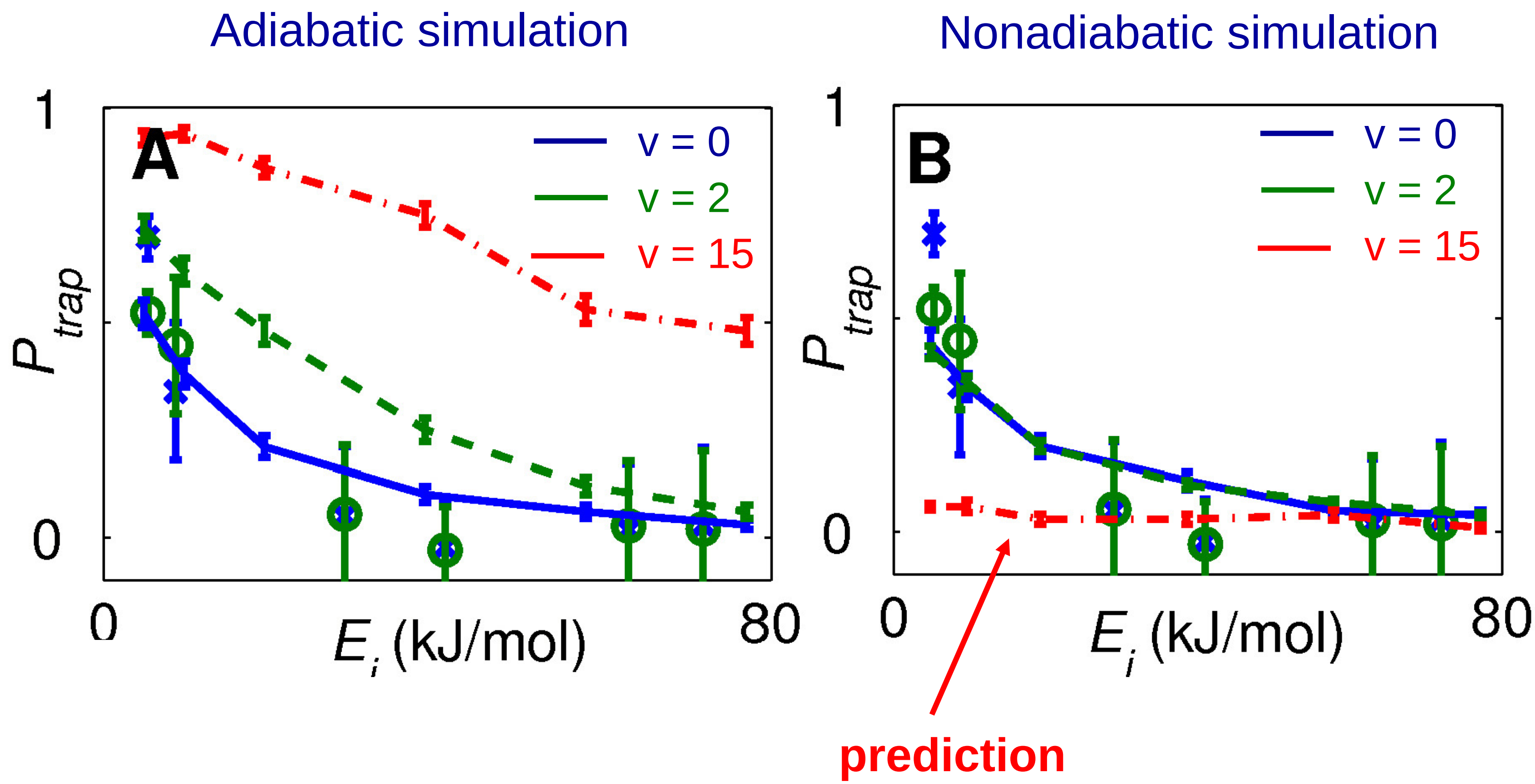


Huang, Rettner, Auerbach, Wodtke, *Science* **2000**, *290*, 111.



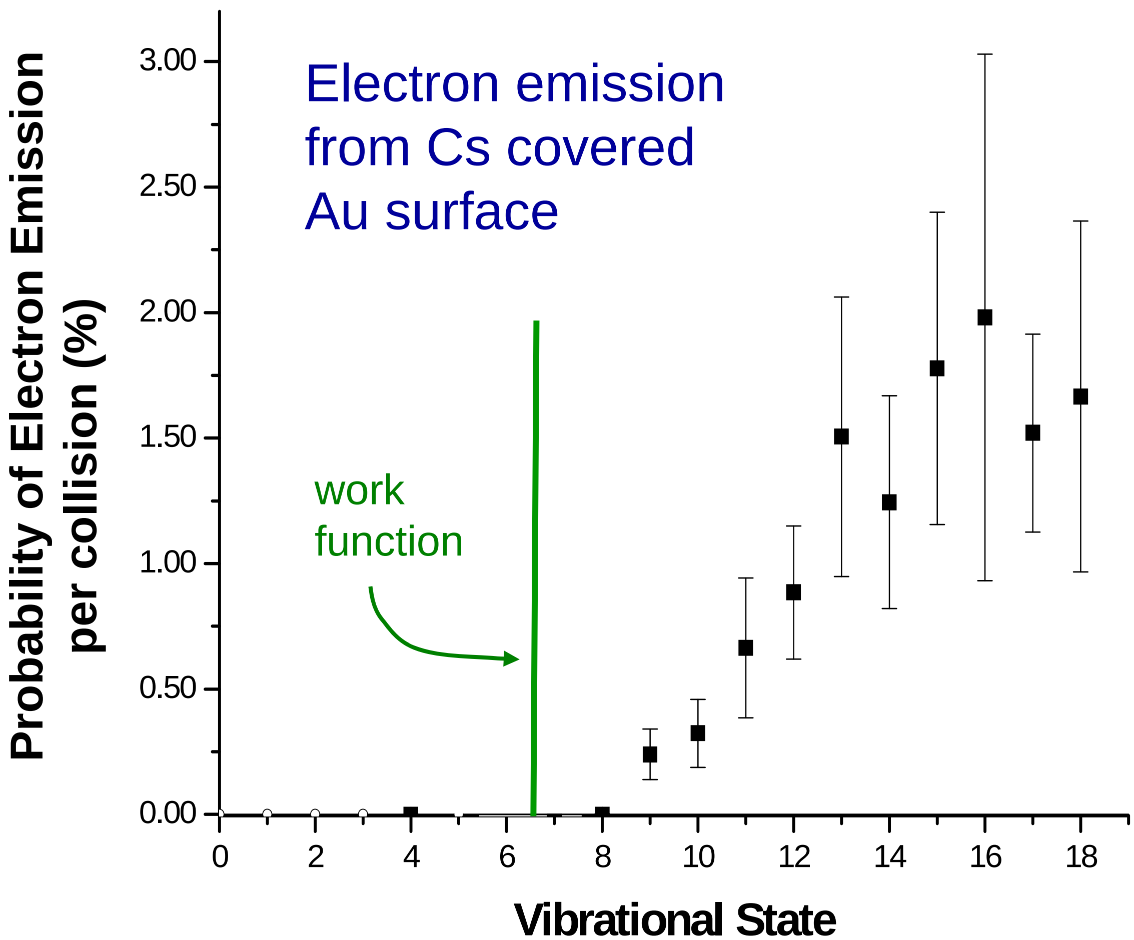
Expts: Huang, Rettner, Auerbach, Wodtke, *Science* **2000**, *290*, 111.

Trapping (sticking) probability



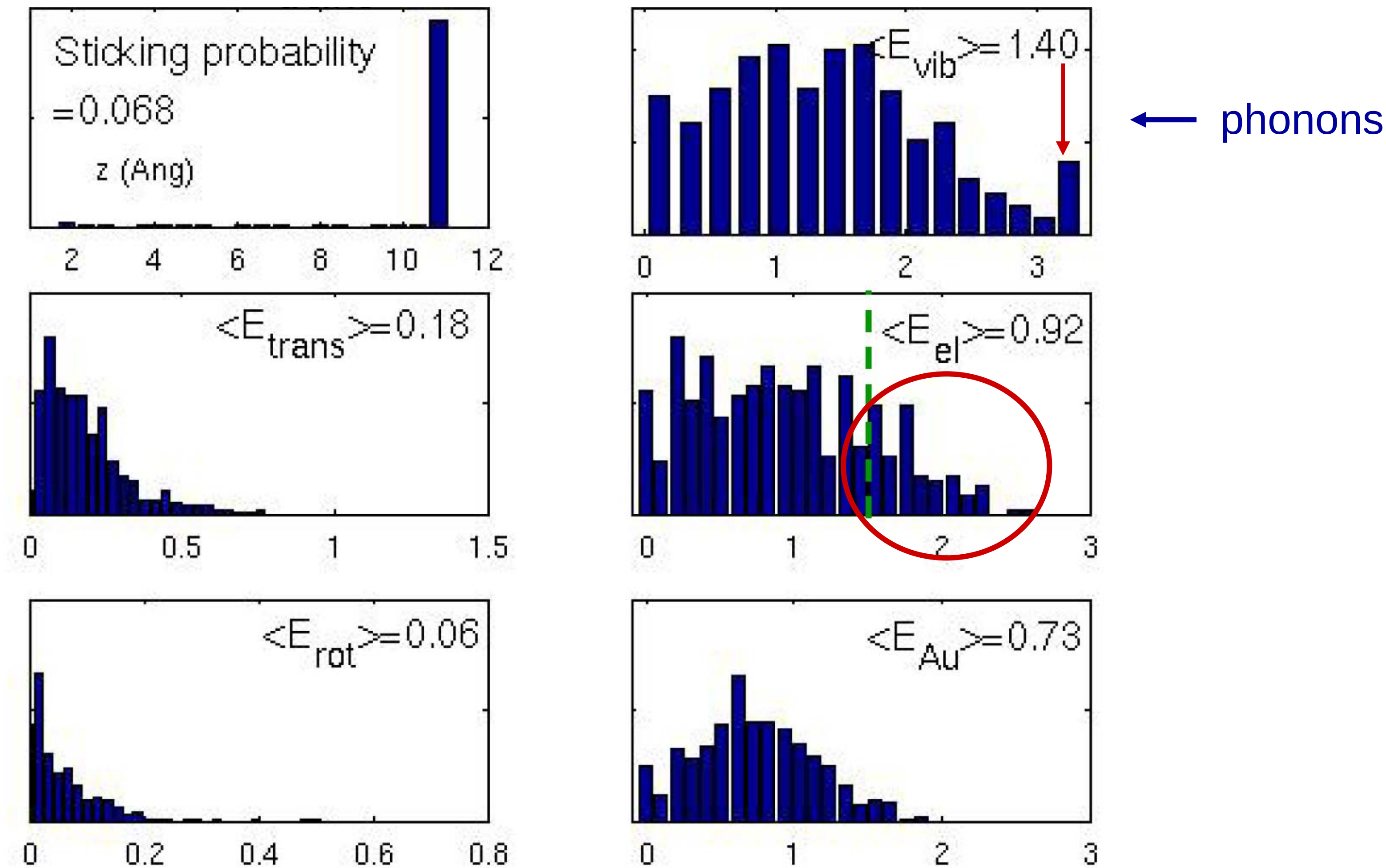
Electron Emission:

→ *inadequacy of electronic friction model ?*



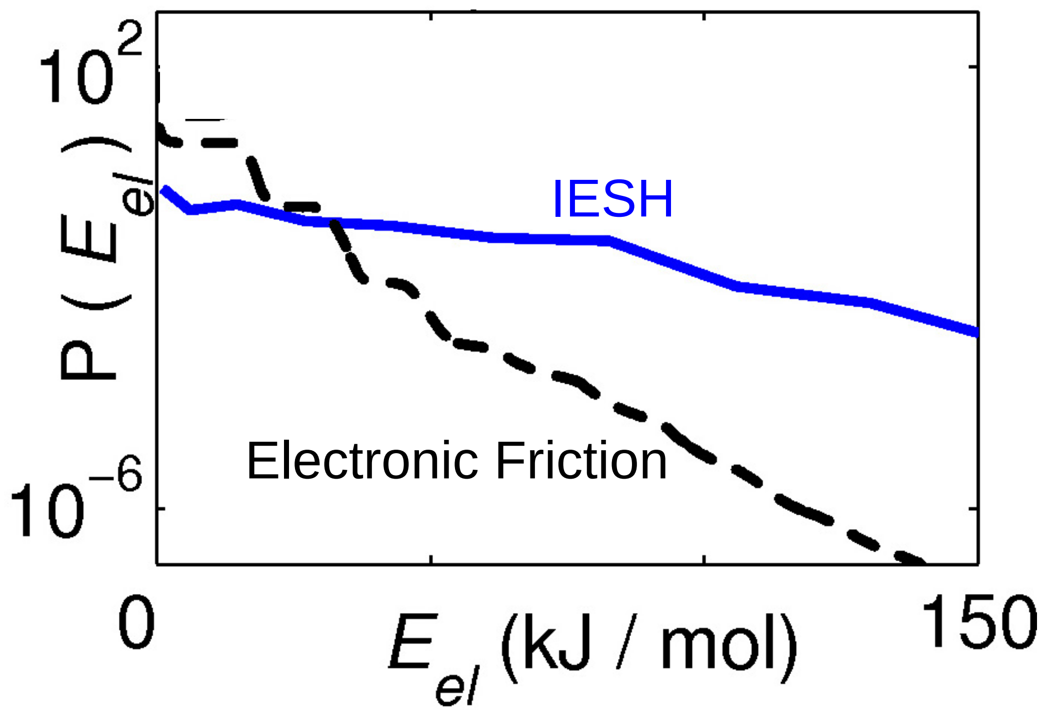
White, J. D.; Chen, J.; Auerbach, D. J.; Wodtke, A. M. *Nature* **2005**, *433*, 503.

NO(v=15) scattered from Au(111) (*2000 trajectories*)



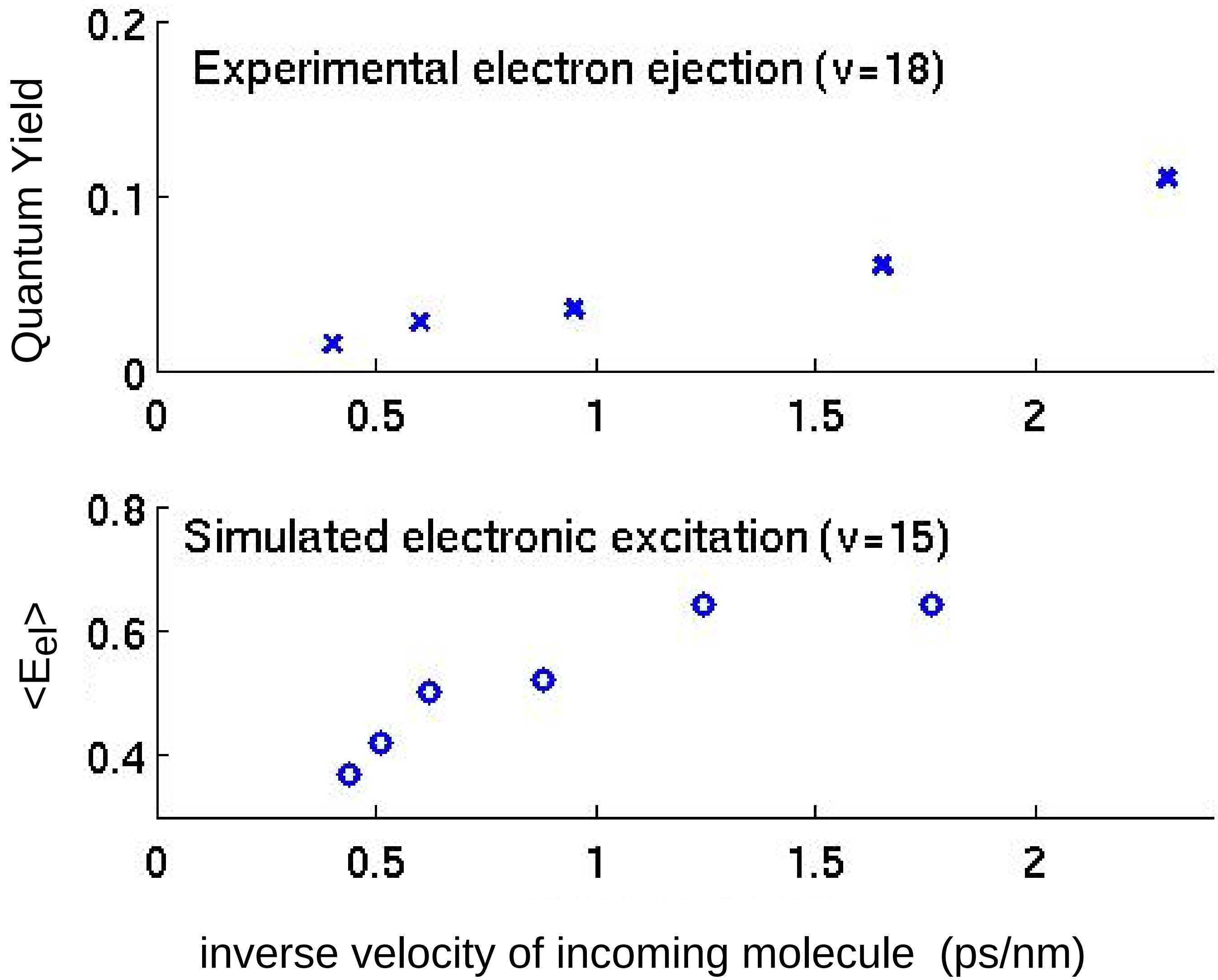
Energy distribution of excited electrons

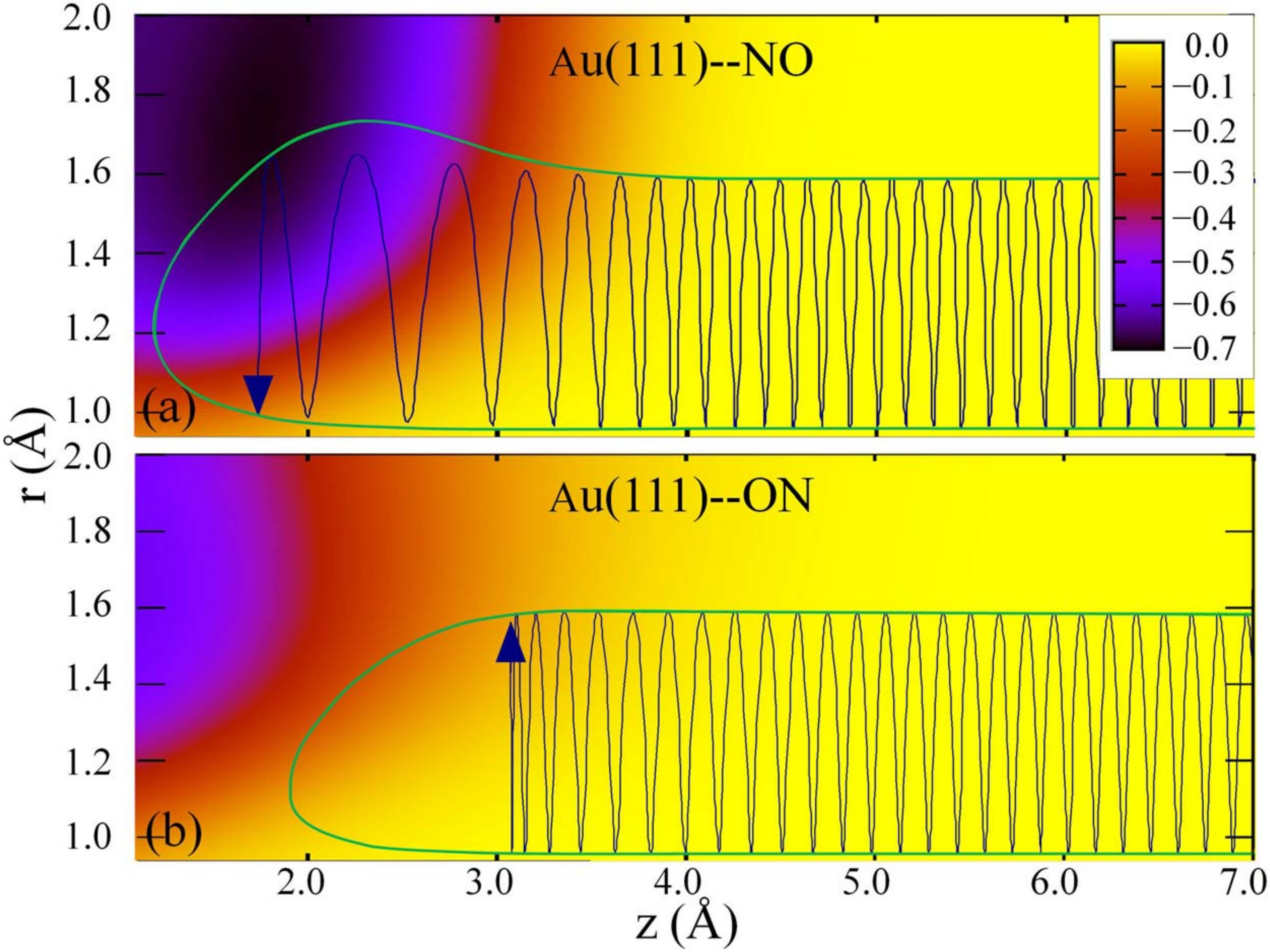
$NO(v=15) \rightarrow Au(111)$



Note: for v=1 where electron transfer is insignificant, IESH and electronic friction models agree quite well.

“Inverse Velocity Dependence of Vibrationally Promoted Electron Emission from a Metal Surface”, Nahler, White, LaRue, Auerbach, Wodtke, *Science* **321**, 1191 (2008)

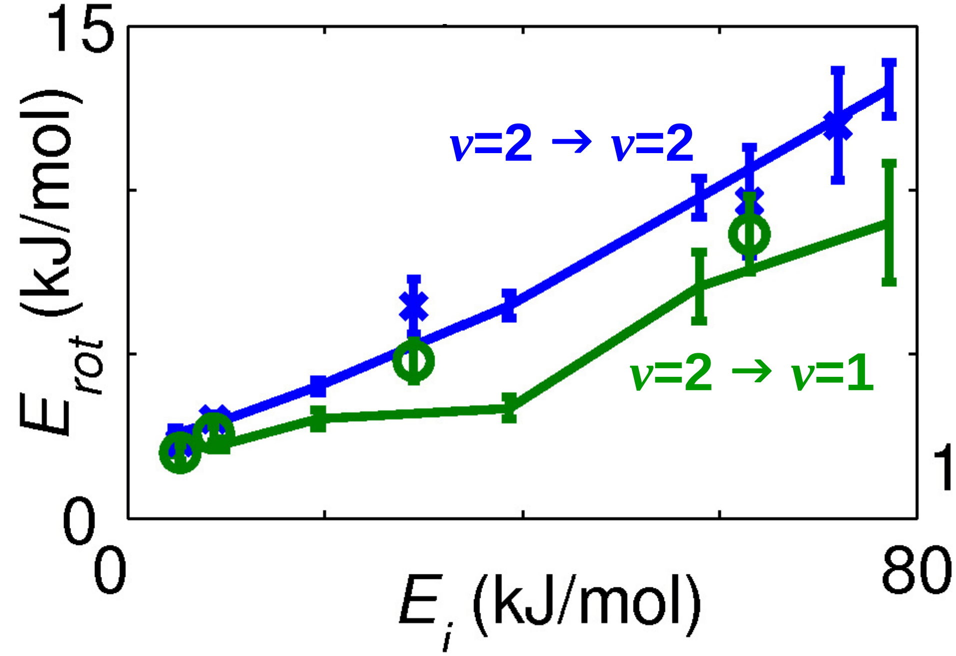




Au(111)--NO
Au(111)--ON
(a)
(b)
r (Å)
z (Å)
2.0
1.8
1.6
1.4
1.2
1.0
3.0
4.0
5.0
6.0
7.0
0.0
−0.1
−0.2
−0.3
−0.4
−0.5
−0.6
−0.7

Final Rotational Energy:

NO(v=2) → Au(111)



Dynamics at Metal Surfaces: Challenges

1. Compute excited state potential energy surfaces and off-diagonal (nonadiabatic) couplings

2. Simulate dynamics subject to multiple (myriads) of potential energy surfaces

Multi-Configuration ?

Constrained DFT ?