Multistate trajectory and statistical theories of spin-forbidden kinetics

Applications in combustion: O+CO, O+C_2H_4, and HNCO

Ahren Jasper

Combustion Research Facility

Sandia National Laboratories

Coworkers

Richard Dawes (MST)

Xiaohu Li and Eugene Kamarchik (Sandia)

$ US DOE BES

Combustion chemistry via "detailed chemical kinetic models"

fuel + O_2 → CO_2 + H_2O

1000s of reactions

Reaction	Kinetic parameters
OH+H2=H2O+H	2.144E8 1.52 3449.
O+OH=O2+H	2.57E13 -0.1589 -479.68
O+H2=OH+H	0.506E+05 2.670 6290.000
H+O2(+M)=HO2(+M)	5.8E11 0.6724 -290
	LOW / 7.2E20 -1.73 536 /
	TROE /0.72 1E-30 1E30 1E30/
	AR/0.5/ H2O/10/ CO2/2/ CH4/3/
OH+HO2=H2O+O2	1.9E16 -1.0 0.0
H+HO2=2OH	1.69E14 0.0 874.
H+HO2=H2+O2	4.28E13 0.0 1411.
H+HO2=O+H2O	3.01E13 0.0 1721.
O+HO2=O2+OH	3.25E13 0.0 0.0
2OH=O+H2O	4.331E3 2.7 -2485.7
CH3+OH=CH3OH	4.498E8 1.3 -54590
. . .	
C3H8+C2H5=C3H7(i)+C2H6	1.51E+00 3.46 7470.0
C3H8+C2H5=C3H7(n)+C2H6	9.03E-01 3.65 9140.0
C3H8+CH2CHCH2=C3H6+C3H7(n)	2.35E+02 3.3 19842.0
C3H8+CH2CHCH2=C3H6+C3H7(i)	7.83E+01 3.3 18169.0
C3H7(n)(+M)=C2H4+CH3(+M)	1.23E+13 -0.1 30202.0
. . .	

T = 300-2000 K

p = 1-100 atm

Kinetic parameters

- Rate coefficients, $k(T,p) = A\ T^n \exp(-E/T)$
- Few from experiment at limited T,p
- Most estimated or empirically "tuned"

Tuned models can predict similar bulk properties with very different chemistry.

Opportunity for predictive theory

- How accurate are theoretical rates? When is theory more accurate than experiment?
- *Accuracy target:* ***factor of ~2***
- Challenging classes of reactions
  1. ***Spin-forbidden chemistry/ISC***
  2. *p dependence/collisional energy transfer*
  3. *Reactions with loose vibrations*
  4. *Complex, multistep reactions*
  5. *etc…*

Spin-forbidden processes (~>) in combustion

Oxidation reactions: $^3O/^3O_2$ + unsaturated singlets

- $^3O + CO \rightarrow {}^3CO_2 \sim\!> CO_2$

  Competes with CO + OH to oxidize CO under some conditions

- $^3O + C_2H_4 \rightarrow {}^{\cdot}CH_2CH_2O^{\cdot} \sim\!>$ oxirane, other singlet species

  Prototype for PAH oxidation; both singlet and triplet products

Radical + radical reactions → singlet & triplet intermediates → various products

- $H + NCO \rightarrow HNCO \sim\!> {}^3HN + CO$

  Relevant to NOx chemistry; NCO otherwise "scrubs" NO

- $H + HO_2 \rightarrow H_2OO \sim\!> {}^3O + H_2O$

  Chain propagating; competes with → 2OH (chain branching)

Methods

Trajectory theories

- E.g., surface hopping, mean-field Ehrenfest, etc.
- We use: Coherent switches with decay of mixing (CSDM)

  "De-mixing" is a semiclassical model for ***electronic decoherence.***

  Validated against quantum scattering for several A+BC systems

Statistical theories

- E.g., "Nonadiabatic Transition State Theory" (P_{hop} = Landau-Zener)
- We have been quantifying the accuracy of this approach & the importance of **multidimensional effects in P_{hop}** and **electronic decoherence.**

Coherent switches with decay of mixing trajectories

- Full-dimensional
- General, global electronic couplings
- No statistical assumptions

Nuclear d.o.f. (classical)

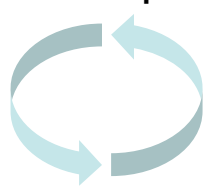
Hamilton's EOM

$$\dot{\mathbf{p}} = -\nabla V_{eff}$$
$$\dot{\mathbf{x}} = \mathbf{p} / \mu$$

mean field $V_{eff} = \sum_{i,j} \rho_{ij} V_{ij}$

surface hopping $V_{eff} = \delta_{iK} V_{ii}$

n-e coupling



Electronic d.o.f. (quantal)

"Classical path" TDSE

$$\Psi_{\text{elec}} = \sum_i c_i \phi_i; \qquad \rho_{ij} = c_i^* c_j$$

$$i\hbar \dot{c}_i = \sum_j c_j V_{ij}(t)$$ *(diabatic) time-dependent Schrödinger equation*

V_{ij} are potentials & diabatic (SO) couplings

$$V_{ij}(t) = V_{ij}(\mathbf{x}(t))$$

There are many methods for coupling the n & e d.o.f.s.
One way is Tully's fewest switches (FS) method.
Our best method is called coherent switches with decay of mixing, CSDM.

Pre-DM equations: Volobuev, Hack, Topaler & Truhlar (2000).

DM equations: Hack & Truhlar, (2001)

CSDM: Zhu, Nangia, Jasper & Truhlar (2004)

Coherent switches with decay of mixing (CSDM)

electronic
populations & coherences

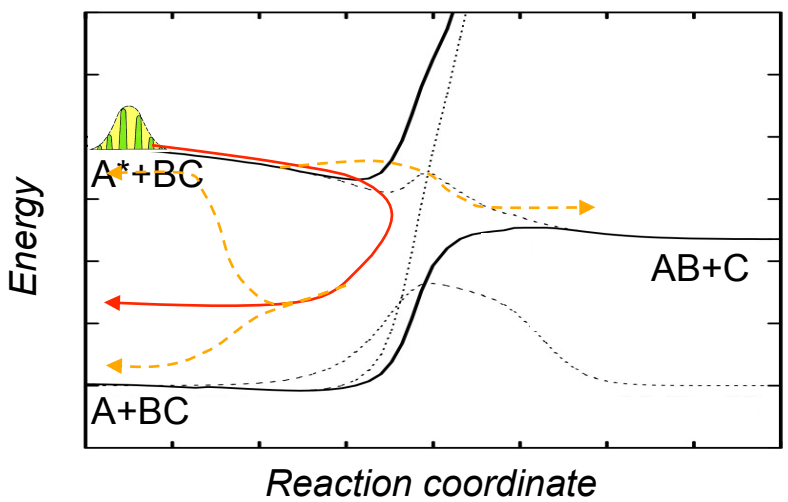
Mean field: $V_{eff} = \sum_{i,j} \rho_{ij} V_{ij}$ potentials & couplings

Original: Semiclassical Ehrenfest (SE)

CSDM: Additional terms in $\dot{\rho}_{ij}$ drive

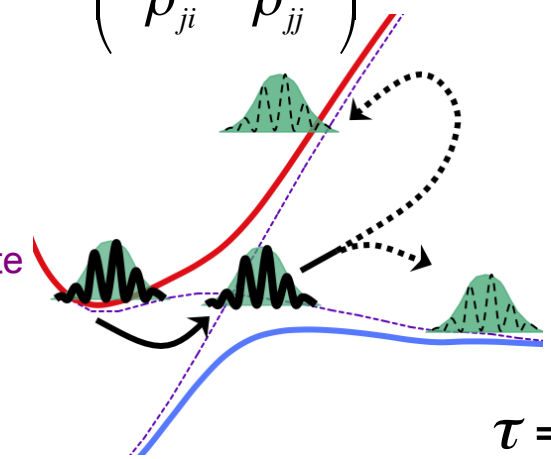
$\rho_{ii} \rightarrow 1$ or 0 as $t \rightarrow \infty$ (de-mixing)

Stochastically, dynamically choose final state based on *locally coherent* electronic motion



Physically,

$$\begin{pmatrix} \rho_{ii} & \rho_{ij} \\ \rho_{ji} & \rho_{jj} \end{pmatrix} \xrightarrow{\text{dephasing}} \begin{pmatrix} \rho'_{ii} & 0 \\ 0 & \rho'_{jj} \end{pmatrix}$$



τ_{deco} from
d overlap / dt
of 1D Gaussian packets

Prezhdo & Rossky 97
Jasper & Truhlar 05

$$\tau = f(F_i - F_j, p_i - p_j)$$

Algorithmically,

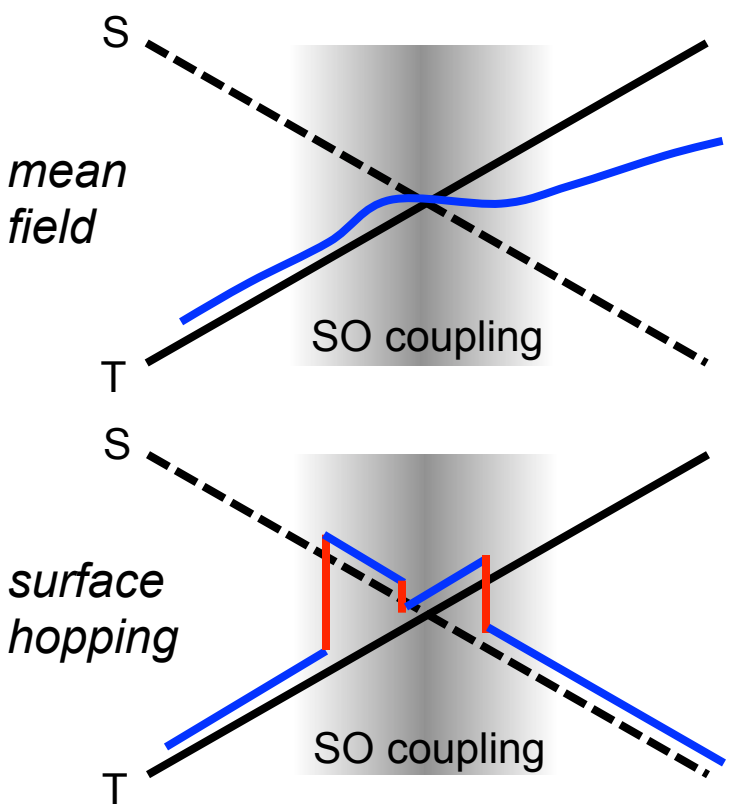
$$\begin{pmatrix} \rho'_{ii} & 0 \\ 0 & \rho'_{jj} \end{pmatrix} \xrightarrow{\text{demixing}}$$

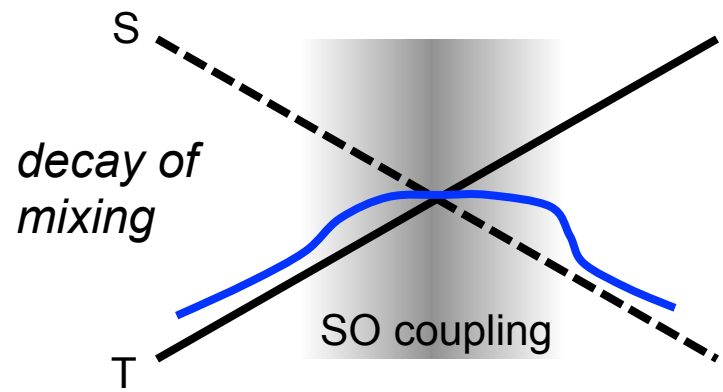
outcome	prob.
$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$	ρ'_{ii}
$\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$	ρ'_{jj}

we choose $k_{demix} \approx 1/\tau_{deco}$

Spin-Forbidden dynamics via Coherent Switches with Decay of Mixing (CSDM) trajectories

Nuclear/electronic coupling: "decay of mixing"
~ mean-field with quantized final states, or
~ surface-hopping with gradual transitions





Validated vs A + BC 3D quantum scattering

Test cases

204 observables (probabilities & internal energies)

3 nonadiabatic interaction types (AC, CI, WC)

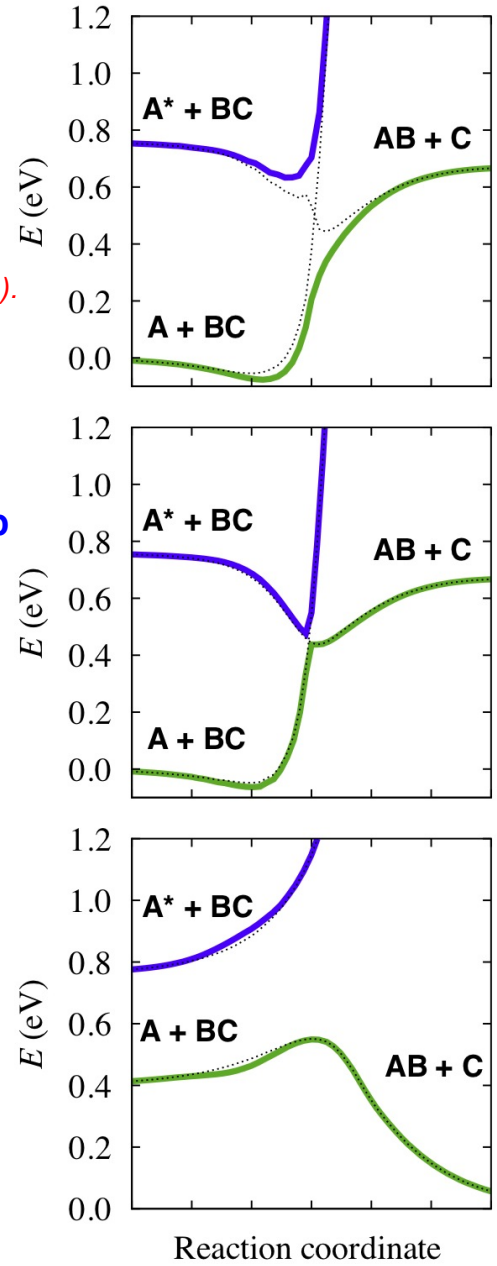
Summarized: Jasper & Truhlar, Adv. Ser. Phys. Chem. 17, 375 (2011).

Mean % errors (best representation)

Mean field	**AC**	**CI**	**WI**	**overall**	**diabatic rep**
SE	74	66	fail	N/A	
CSDM	**21**	**33**	**18**	**24**	**25**
Surface hopping					
FS	53	40	29	41	**125**
FSTU	38	39	25	34	**66**

"improved" FS to handle frustrated hops

+ errors due to the PES and couplings!



AC: Avoided crossing
e.g., Na + FH

CI: Conical intersection
e.g., Na + H_2

WI: Weak interaction
e.g., Br + HR

Very accurate coupled potential surfaces for CO_2

Richard Dawes

Quantum chemistry: dw-MR(12e,10o)CI+Q/CBS(avtz,avqz)

Near full valence + large basis CBS + "dynamic" state weights = very accurate

	exp	calc	
$^3O \rightarrow {}^1O$	45.4	45.1	kcal/mol
$CO_2 \rightarrow {}^3O + CO$	125.9	125.8	kcal/mol

Fitted surfaces via IMLS (Dawes, Al Wagner, & Don Thompson)

- Interpolated from *N* (= 1500, e.g.) MRCI energies; fit passes through these data
- Automated scheme for adding ab initio data to minimize interpolation errors
- Tradeoff: IMLS surfaces built from ~*N* local expansions, increases cost
  Converges to "direct dynamics" as *N* increases
- IMLS is intermediate of "analytic" surfaces and direct dynamics
- For large enough *N*, IMLS is very efficient direct dynamics

CO_2 model

1 singlet S

2 triplets T1 and T2

2 coupling surfaces: $\varepsilon_1 = \langle S|H_{SO}|T1\rangle$

$\varepsilon_2 = \langle S|H_{SO}|T2\rangle$

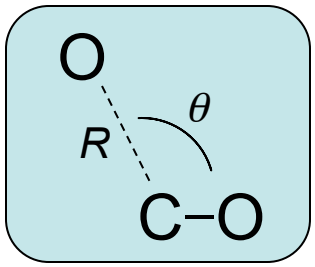
Coupled diabatic representation

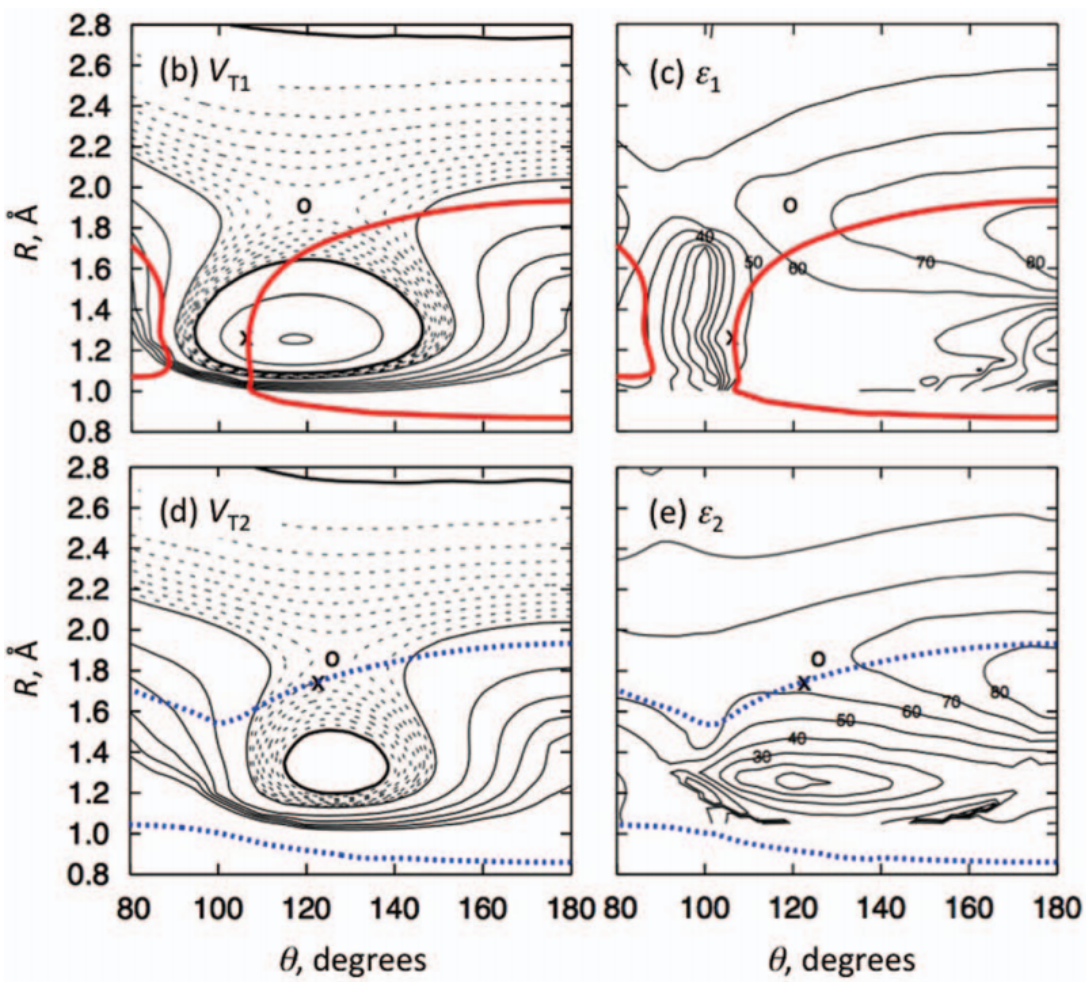
$$\tilde{\tilde{V}}(\mathbf{R}) = \begin{pmatrix} \mathbf{S} & \varepsilon_1 & \varepsilon_2 \\ \varepsilon_1 & \mathbf{T1} & 0 \\ \varepsilon_2 & 0 & \mathbf{T2} \end{pmatrix}$$

Coupled diabatic PESs for $^3O + CO \rightarrow CO_2$

Two reactive triplet surfaces T1 and T2

Two spin-orbit coupling surfaces <S|H_{SO}|T1>, <S|H_{SO}|T2>





SO coupling varies along the seam

40-80 cm^{-1}

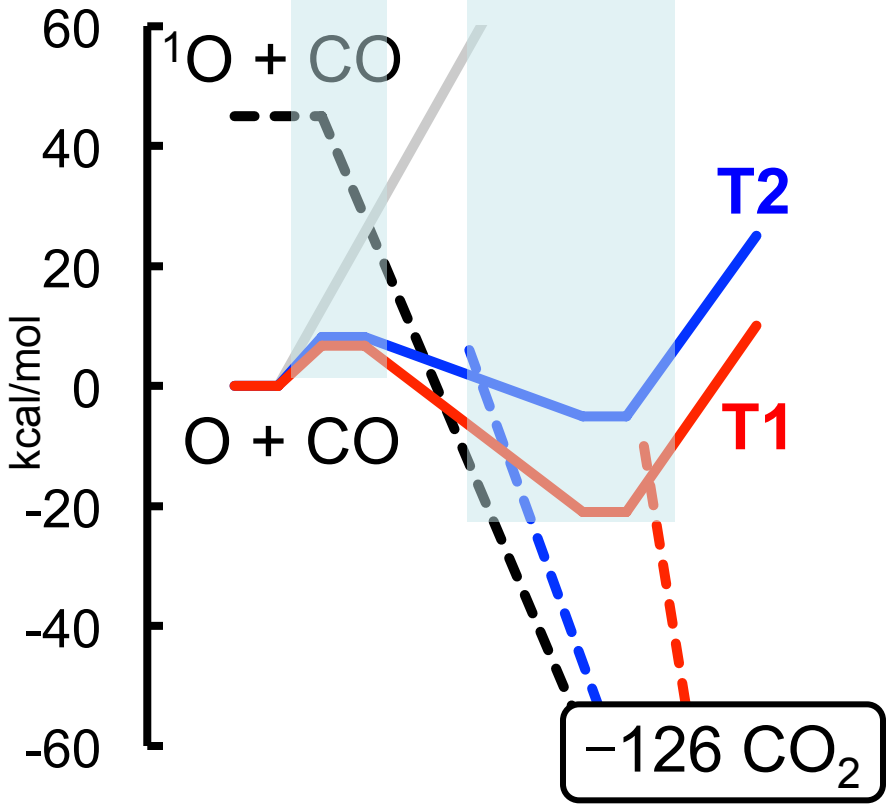
60-80 cm^{-1}

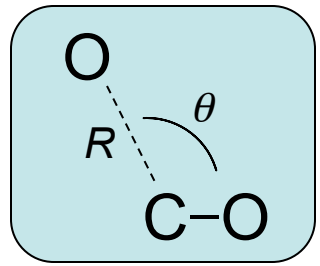
$P_{hop} \sim SO^2$

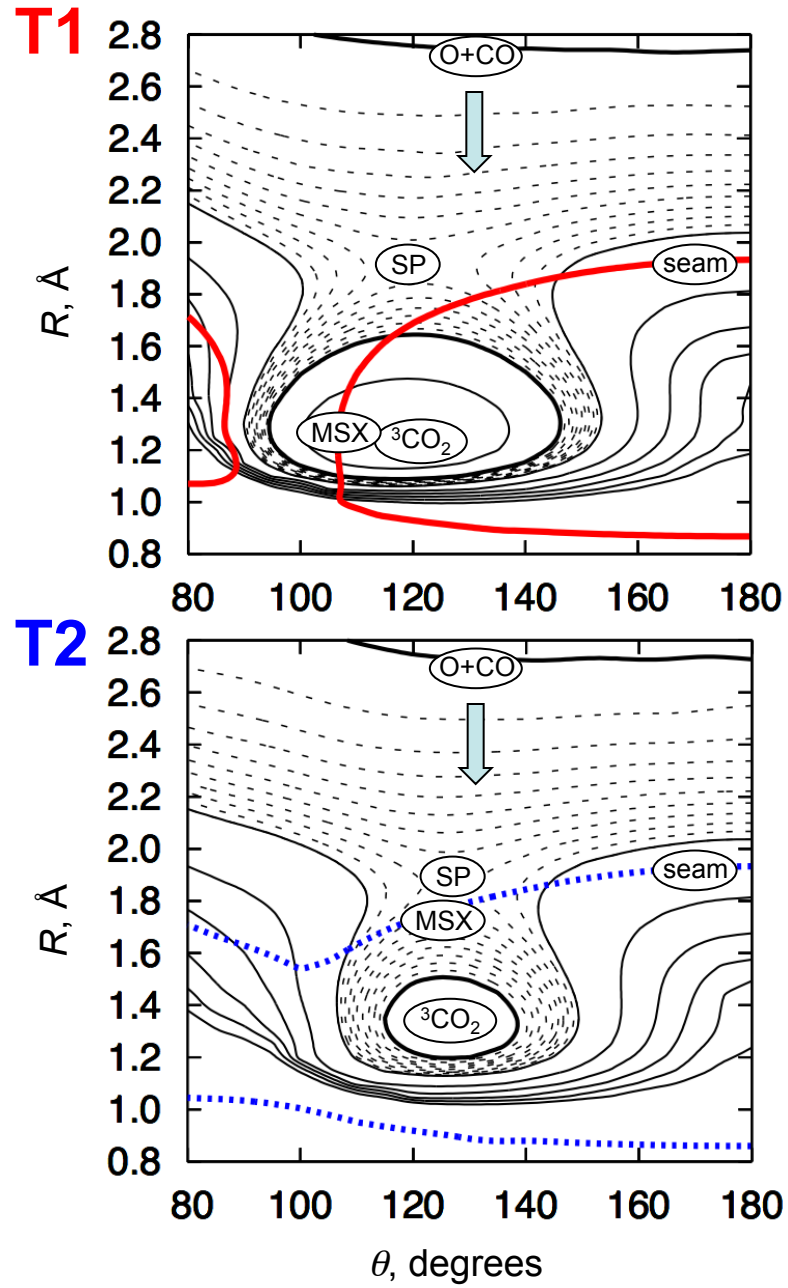
Trajectories can quantify nonstatistical effects

Two TS model?

$$N_{2TS}^{-1} = N_{SP}^{-1} + N_{MSX}^{-1}$$







Crossing seams are not transition states

Miller's unified statistical theory

Unified statistical model for "complex" and "direct" reaction mechanisms*

William H. Miller†

The Journal of Chemical Physics, Vol. 65, No. 6, 15 September 1976

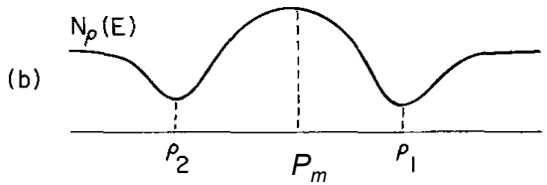


FIG. 5. The flux integral $N_\rho(E)$ through surface S_ρ, as a function of ρ, for a potential surface of the type in (a) Fig. 1 and (b) Fig. 2.

$$\frac{1}{N} = \frac{1}{N_1} + \frac{1}{N_2} - \frac{1}{N_m}$$

0

statistical

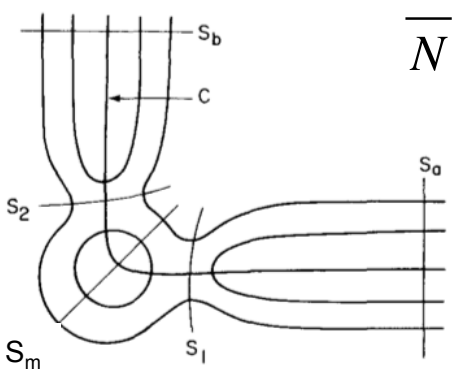
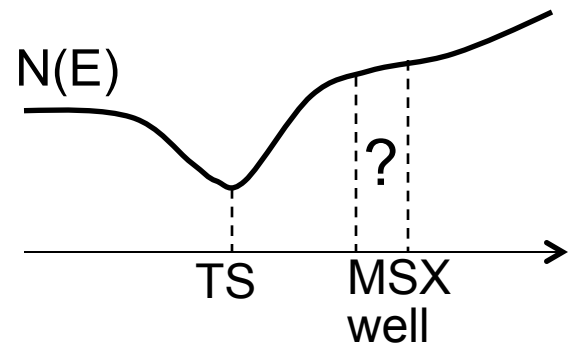
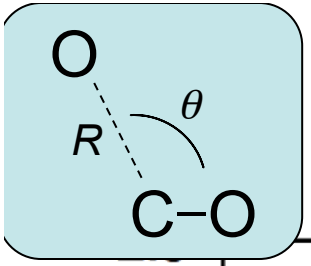


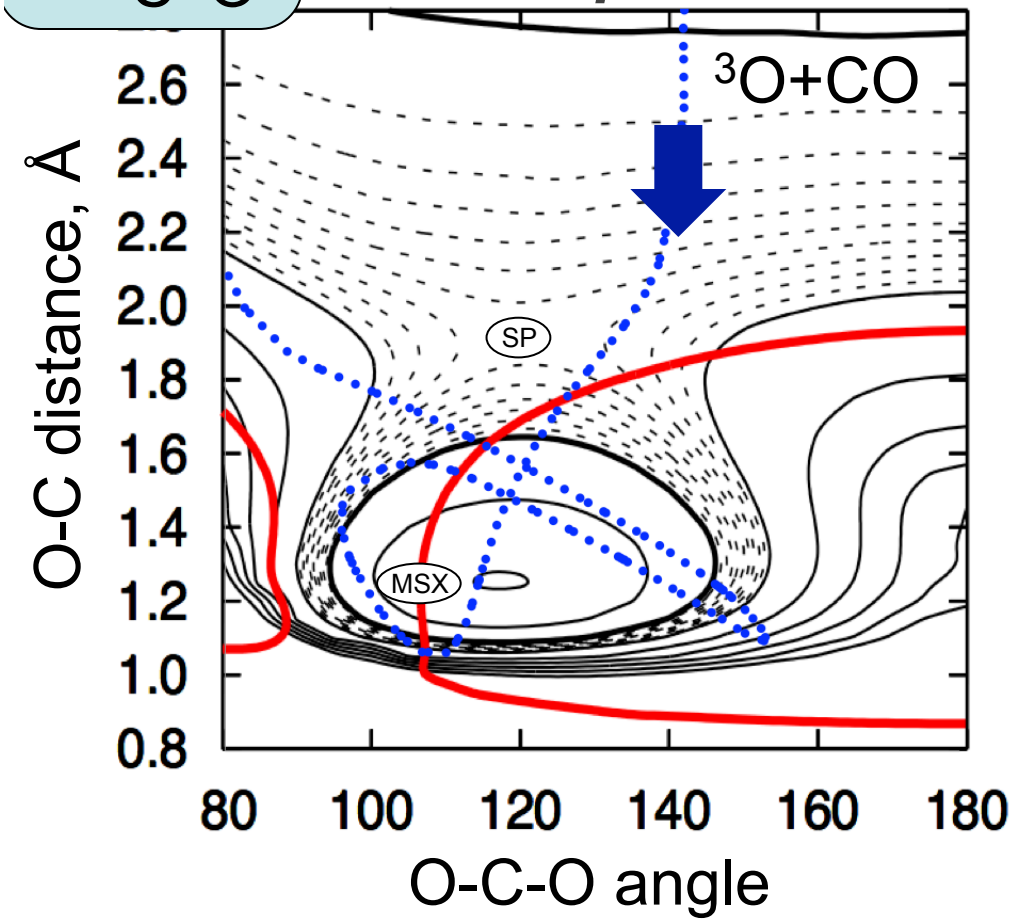
FIG. 2. Sketch of a potential energy surface for a collinear A+BC → AB+C reaction that has an attractive well, corresponding to a stable ABC molecule, that is separated from reactants and products by saddle points. Curve C is the reaction path, and the dividing surfaces S_1 and S_2 cross it through the saddle points, S_x through the minimum of the potential well, and S_a and S_b in the reactant and product regions, respectively.

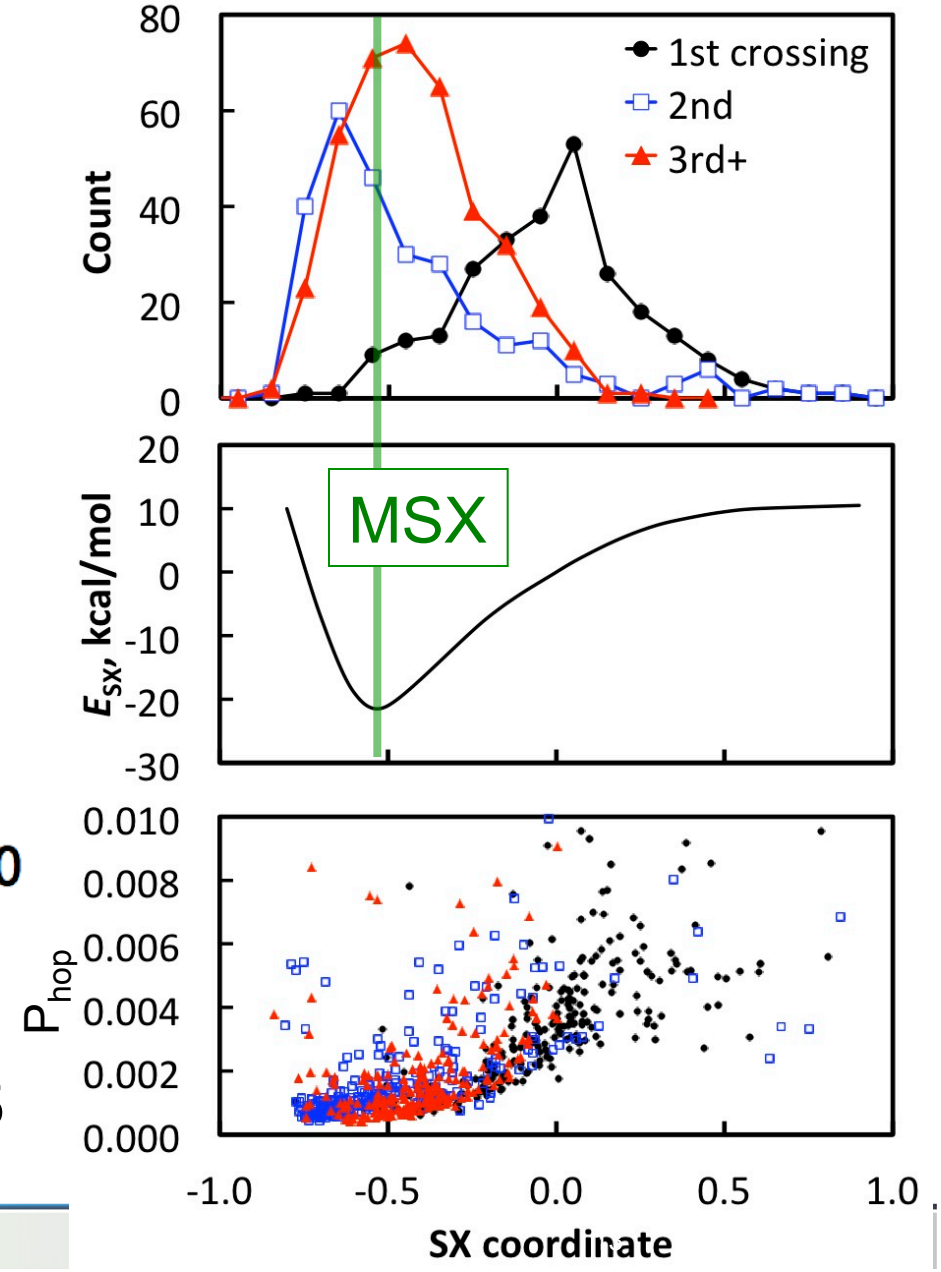


$^3O + CO$



First triplet PES



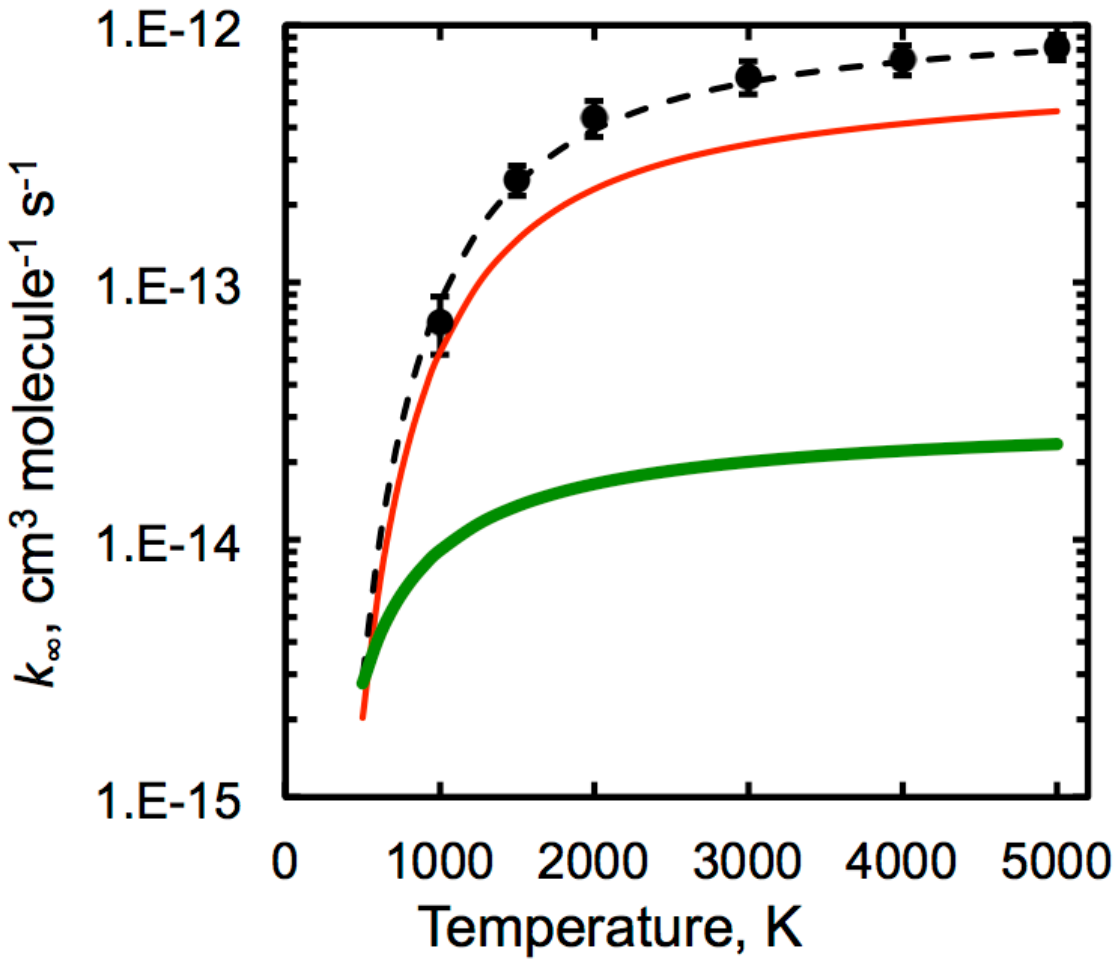


	$10^3 \langle P_{hop} \rangle$
1/4 direct	**3.4**
1/4 intermediate	**1.8**
1/2 statistical	**2.3**

$$10^3 \langle P_{hop} \rangle_{all} = 2.5$$

High pressure limit

$^3O + CO \sim> CO_2$



CSDM

NA TST (w/ 1D LZ)

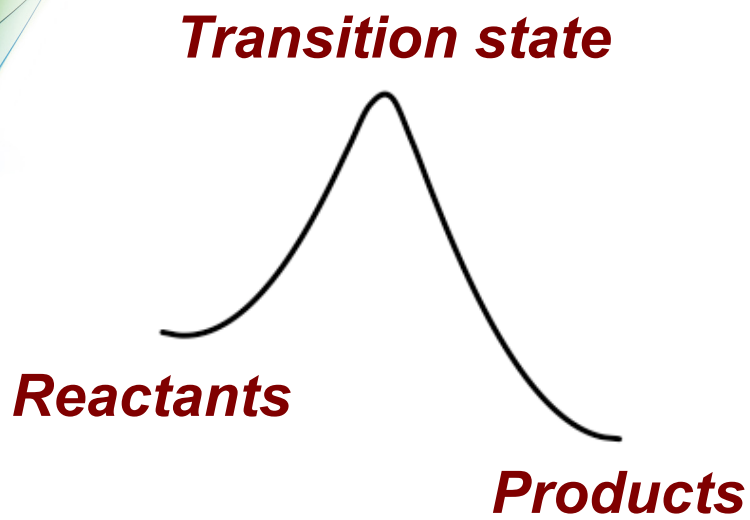
2x?

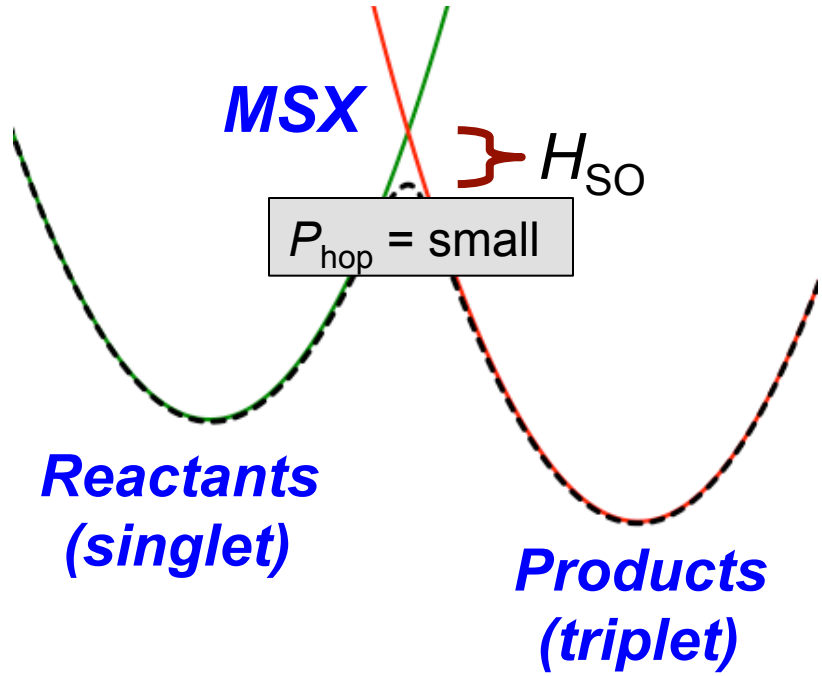
Up to 35x!

Estimate in many combustion models (1975)

Nonadiabatic "transition state theory"

Recent: Harvey, Morokuma, etc…





$$k_{\mathrm{TST}}(T) = \frac{\sigma_{rot}}{hQ_{reac}} e^{-V^{\neq}/k_B T} \int dE\, e^{-E/k_B T} N^{\neq}(E)$$

$V^{\neq}$: threshold energy

$N^{\neq}$: state count at the TS

P_{reac} = 1 at the TS is the *fundamental assumption* of TST

$$k_{NA}(T) = \frac{\sigma_{rot}}{hQ_{reac}} e^{-V_X/k_B T} \int dE\, e^{-E/k_B T} N_{NA}(E)$$

V_X : threshold energy

N_X : state count at the x-ing

$$N_{NA}(E) = \int d\varepsilon\, N'_X(\varepsilon)\, P_{hop}(E-\varepsilon)$$

H_{SO} SO coupling

$|\nabla V|$ | grad of the gap |

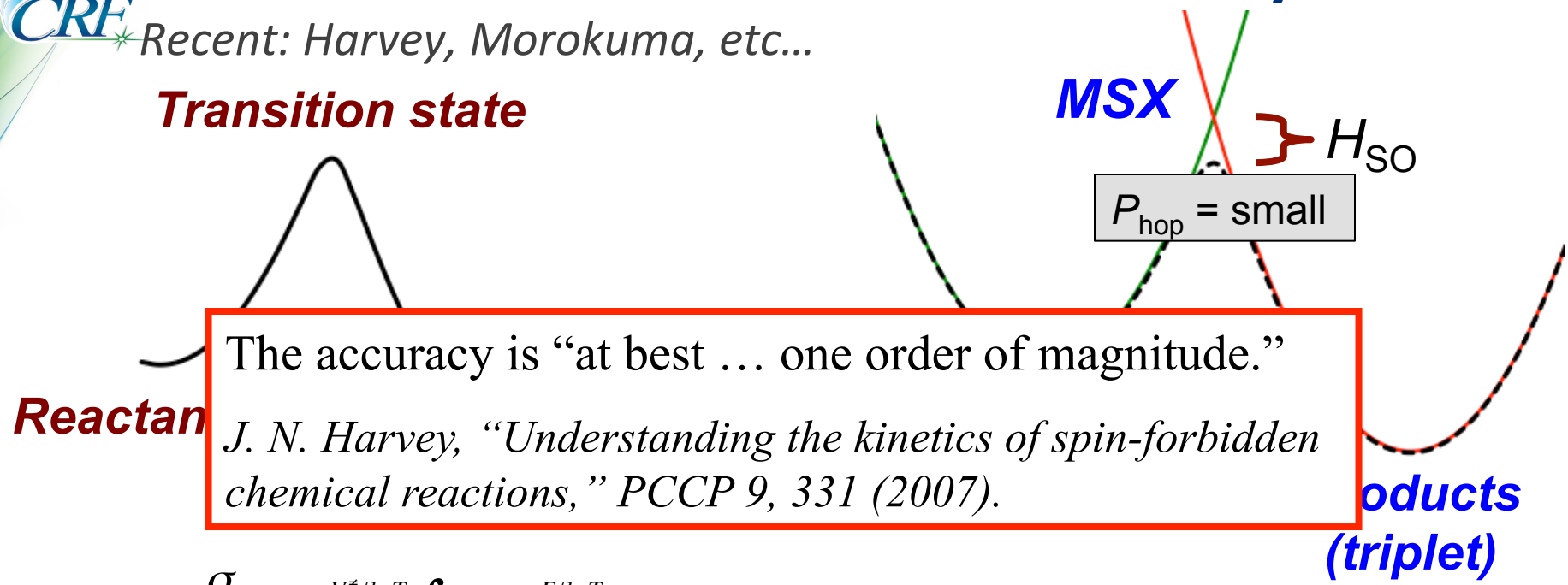
$E_\perp$ energy along ∇V

$P_{hop} = 2\, P_{LZ}$

$$P_{LZ}(E_\perp) \approx \frac{-2\pi H_{SO}^2}{\hbar |\nabla V| \sqrt{2E_\perp/\mu}}$$

Nonadiabatic "transition state theory"

Recent: Harvey, Morokuma, etc…



The accuracy is "at best … one order of magnitude."

J. N. Harvey, "Understanding the kinetics of spin-forbidden chemical reactions," PCCP 9, 331 (2007).

$$k_{\mathrm{TST}}(T) = \frac{\sigma_{rot}}{hQ_{reac}} e^{-V^{\neq}/k_B T} \int dE\, e^{-E/k_B T} N^{\neq}(E)$$

$V^{\neq}$: threshold energy

$N^{\neq}$: state count at the TS

P_{reac} = 1 at the TS is the *fundamental assumption* of TST

$$k_{\mathrm{NA}}(T) = \frac{\sigma_{rot}}{hQ_{reac}} e^{-V_X/k_B T} \int dE\, e^{-E/k_B T} N_{\mathrm{NA}}(E)$$

V_X : threshold energy

N_X : state count at the x-ing

$$N_{\mathrm{NA}}(E) = \int d\varepsilon\, N'_X(\varepsilon)\, P_{\mathrm{hop}}(E-\varepsilon)$$

H_{SO} SO coupling

$|\nabla V|$ | grad of the gap |

$E_{\perp}$ energy along ∇V

$P_{\mathrm{hop}} = 2\, P_{\mathrm{LZ}}$

$$P_{\mathrm{LZ}}(E_{\perp}) \approx \frac{-2\pi H_{\mathrm{SO}}^2}{\hbar |\nabla V| \sqrt{2E_{\perp}/\mu}}$$

Nonadiabatic "~~transition state theory~~" statistical theory

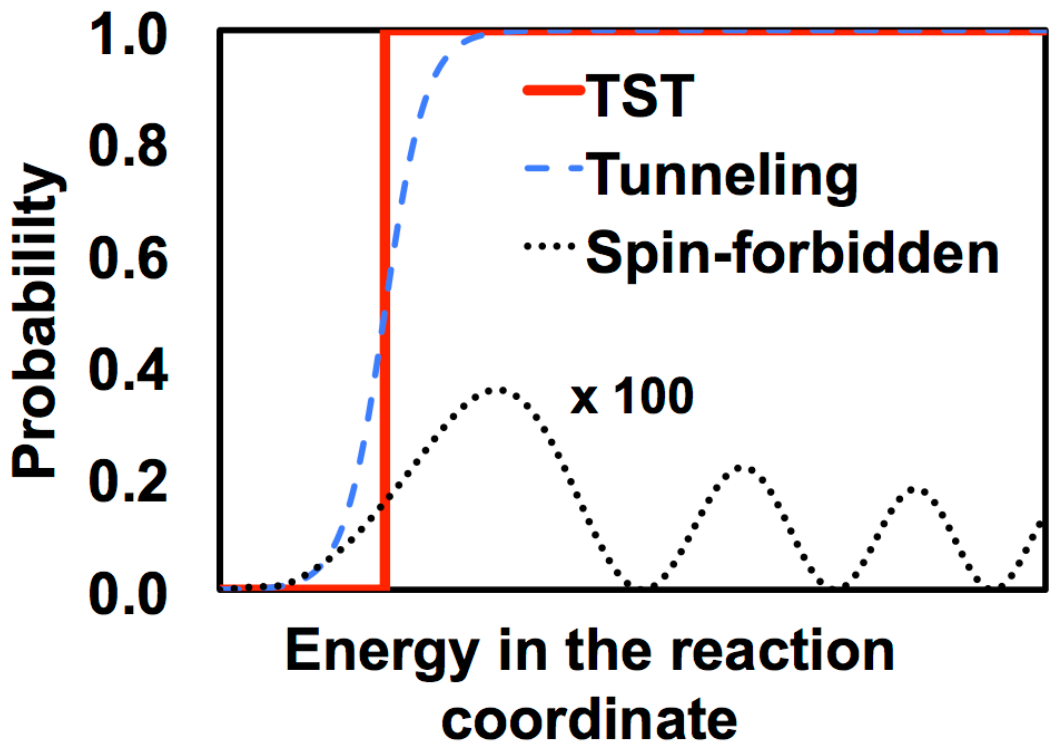
1. The crossing seam is not a transition state

2. Within the statistical model, missing multidimensional effects in P_{hop}

a. static: H_{SO}, etc, vary along the seam; P_{hop} depends on localtion on the seam

b. dynamical: P_{hop} depends on E_{perp} and E (total)

c. nonlocal: One-dimensional "weak coupling" low-E_{perp} limit may not apply



Double passage P_{hop} in one dimension: Adiabatic vs weak coupling low-E_{perp} limit

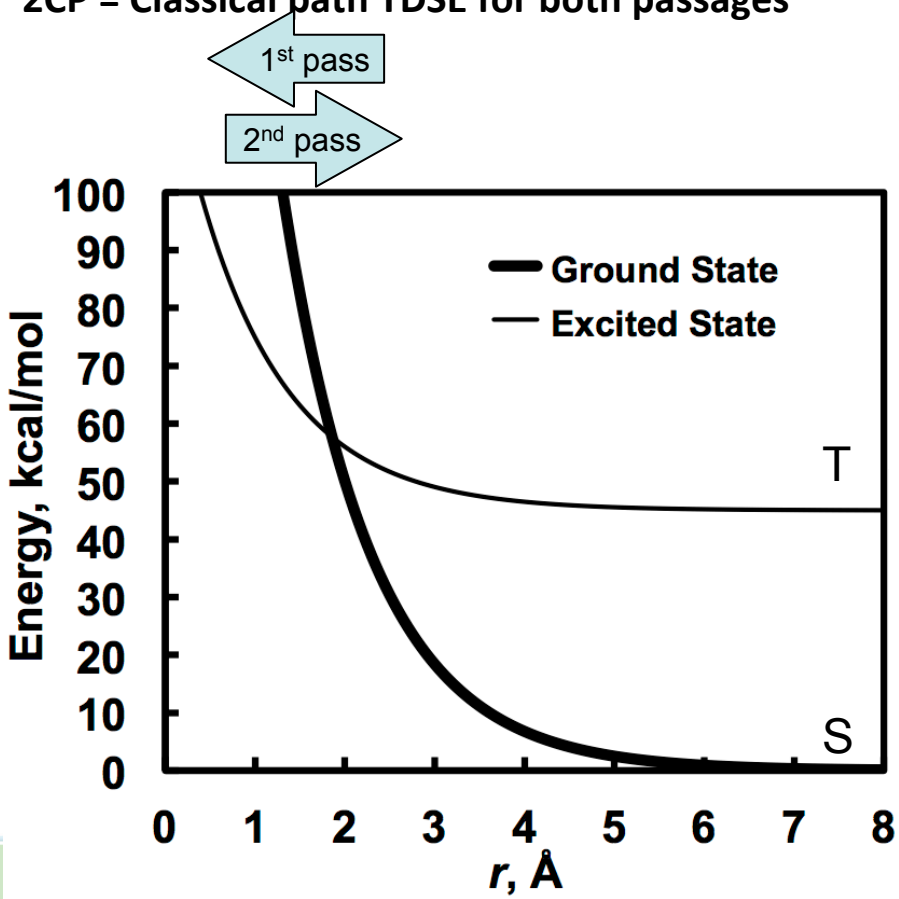
Model 1D system based on the CO_2 S/T1 MSX

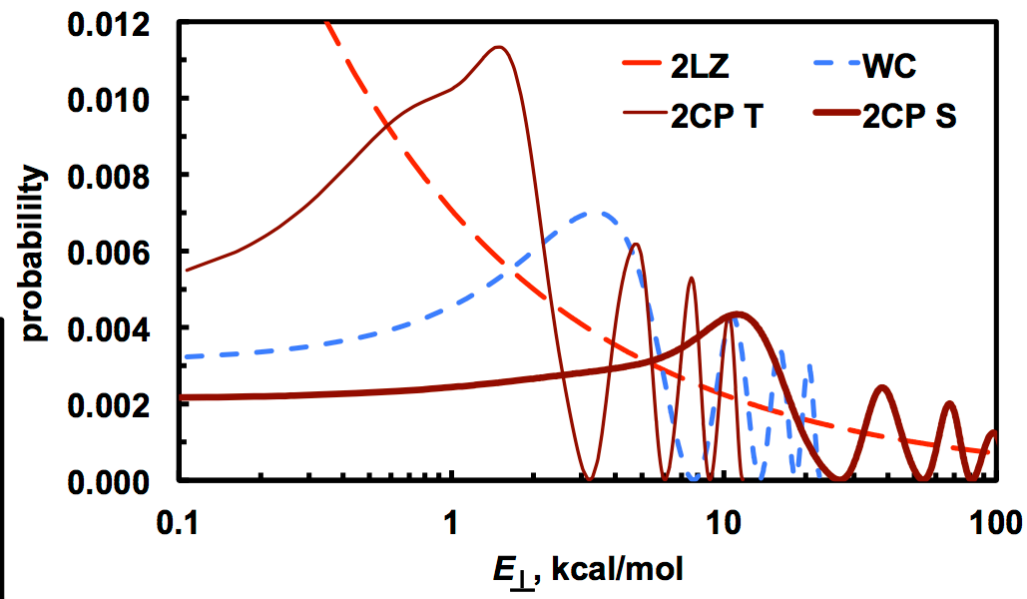
2LZ = "double passage" Landau-Zener P_{2LZ} = 1 at low E_{perp}

WC = "Airy" formula, Nikitin, Child, Delos, etc…

2 passes e- phases interfere

2CP = Classical path TDSE for both passages





Double passage P_{hop} in one dimension: Adiabatic vs weak coupling low-E_{perp} limit

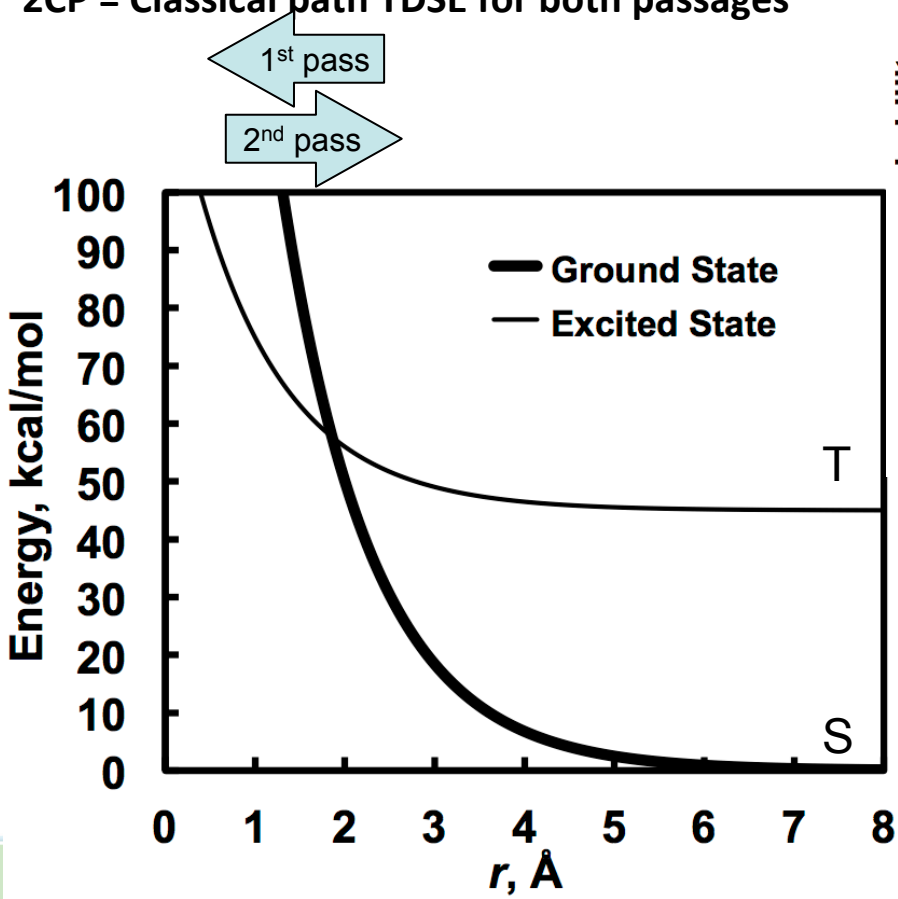
Model 1D system based on the CO_2 S/T1 MSX

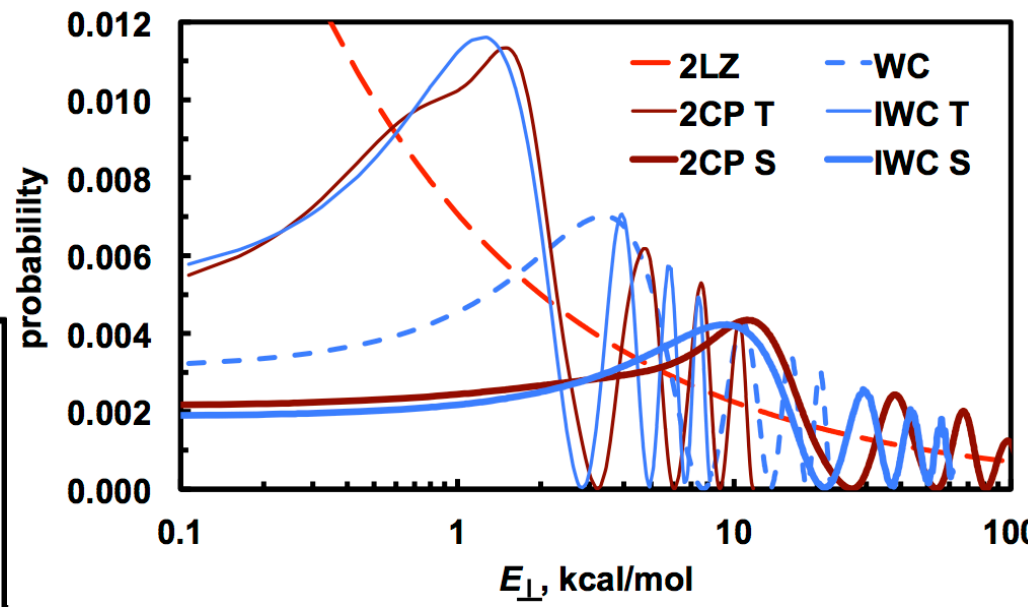
2LZ = "double passage" Landau-Zener P_{2LZ} = 1 at low E_{perp}

WC = "Airy" formula, Nikitin, Child, Delos, etc…

2 passes e- phases interfere

2CP = Classical path TDSE for both passages





IWC = small modification to WC

IWC = 2CP

Single passage P_{hop} in one dimension

LZ = Landau-Zener

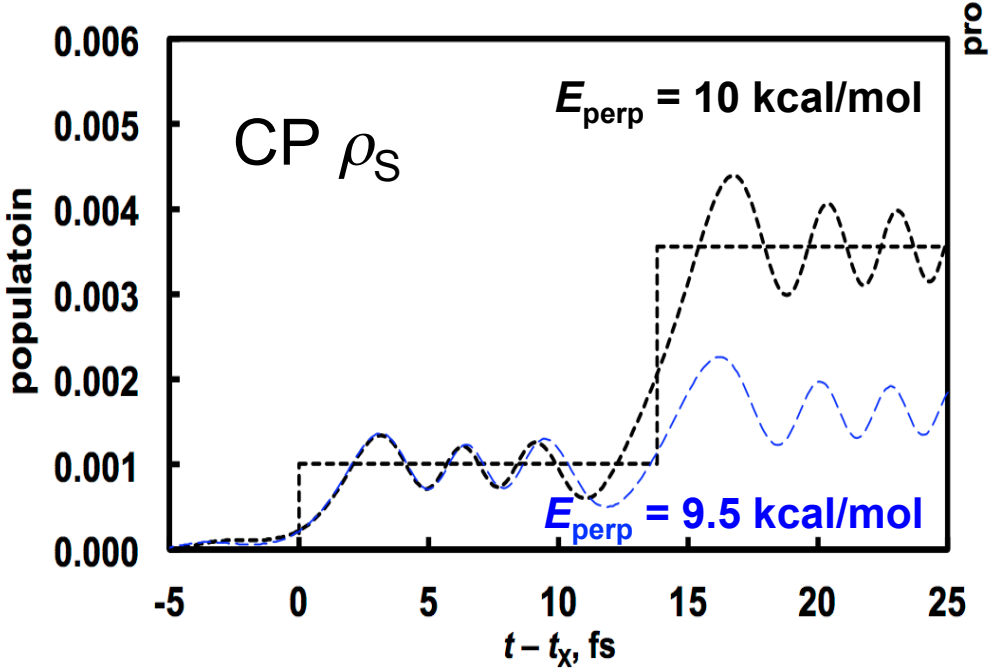
WC/2 = "Airy" formula, Nikitin, Child, Delos, etc…

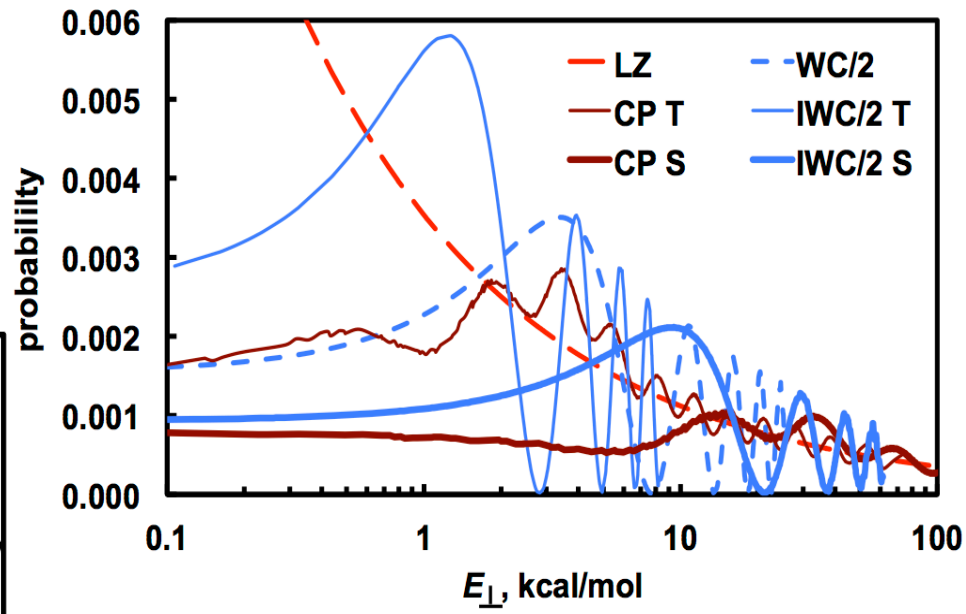
"adiabatic" limit vs "weak coupling" limit

CP = Classical path TDSE

IWC/2 = Depends on occupied electronic state

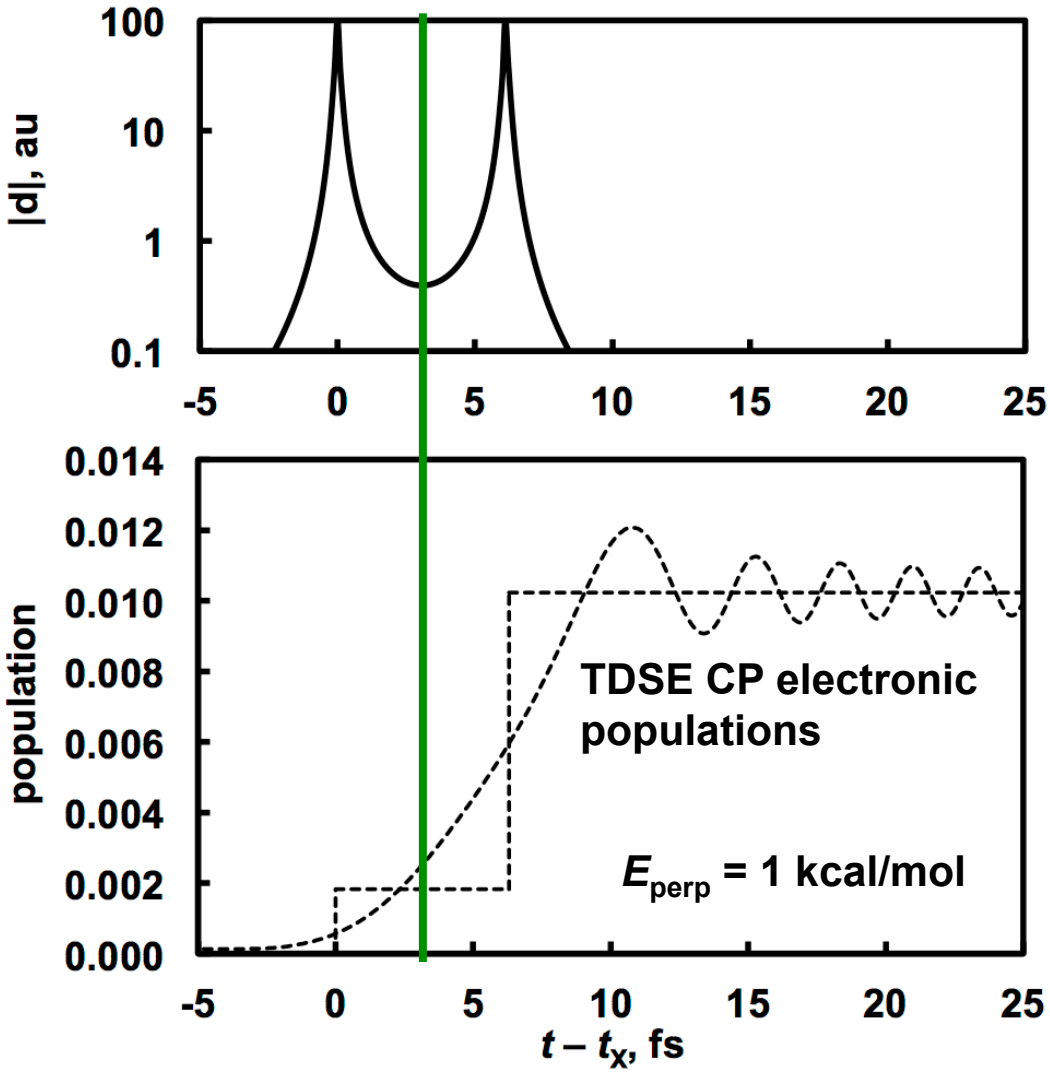
CP ≠ IWC/2





Single passage P_{hop} in one dimension at low E_{perp}

The interaction region for each passage can be defined using the nonadiabatic coupling vector, d = <S|$\nabla_{nuclear}$|T>



Single passage or double passage?

Semiclassical model

1. Coherent single passages
2. Decoherence allowed **between passages**
3. Decoherence probability:

$$1-\exp(-\Delta t_X/\tau_{deco})$$

Fast decoherence => single passage

For CO_2: $\tau_{deco} < \Delta t_X$

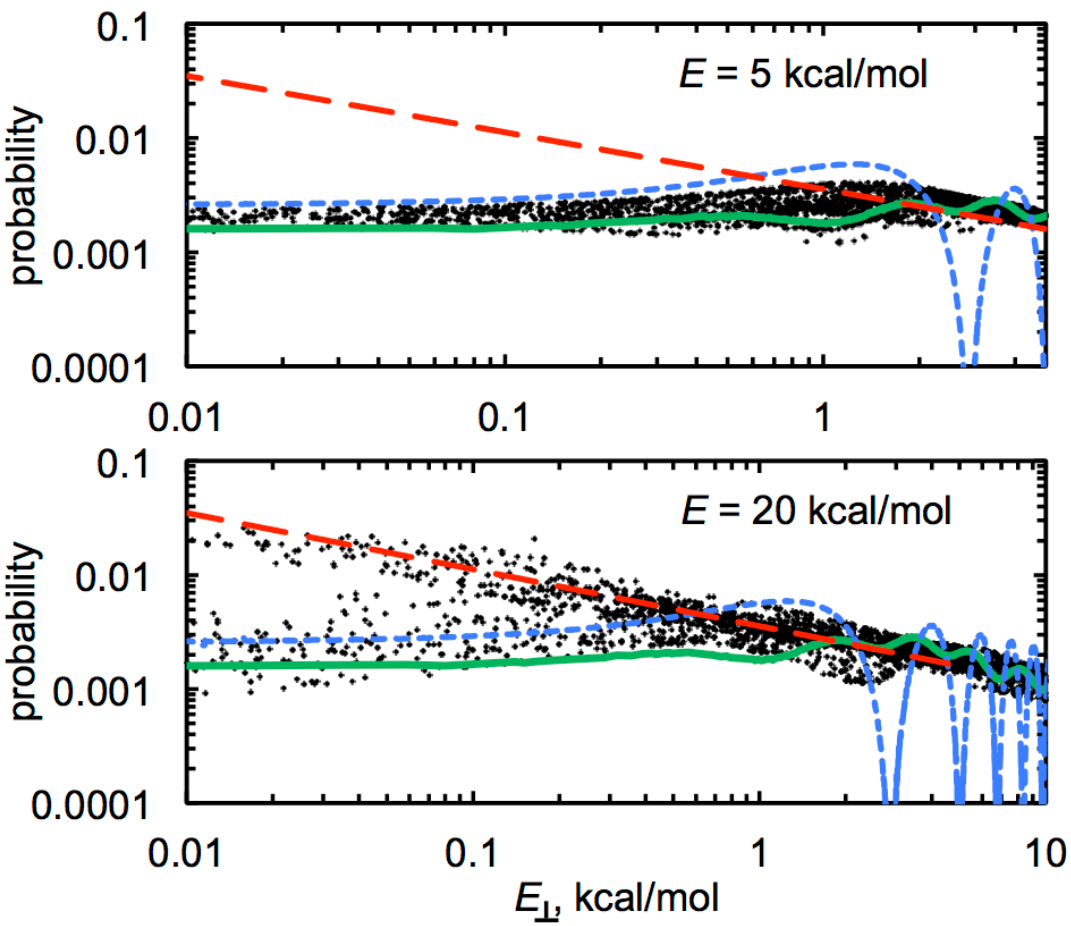
Multidimensional single-passage P_{hop}

Artificial ensemble of CO_2 trajectories all crossing at the MSX

no "static" multidimensional effects

"dynamic" and "nonlocal" multidimensional effects included via CP TDSE

*Full-D CP probabilities are **not** single-valued in E_{perp} AND **depend on E** (total)*



LZ

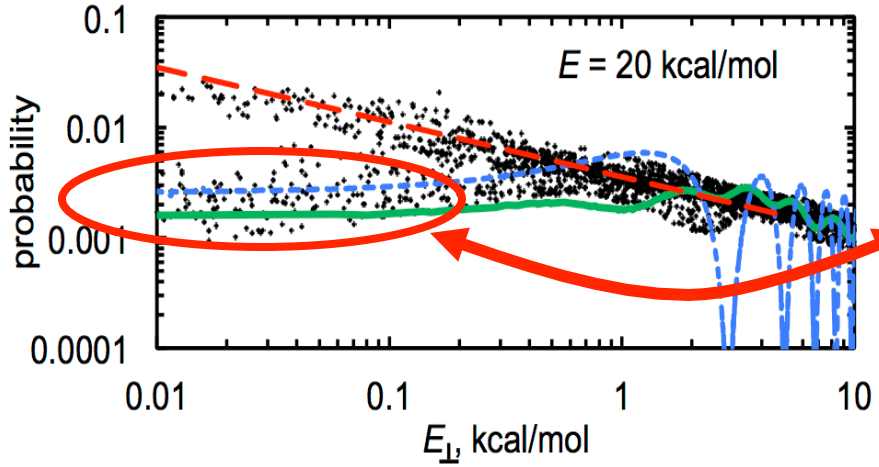
IWC/2

1D CP

CP

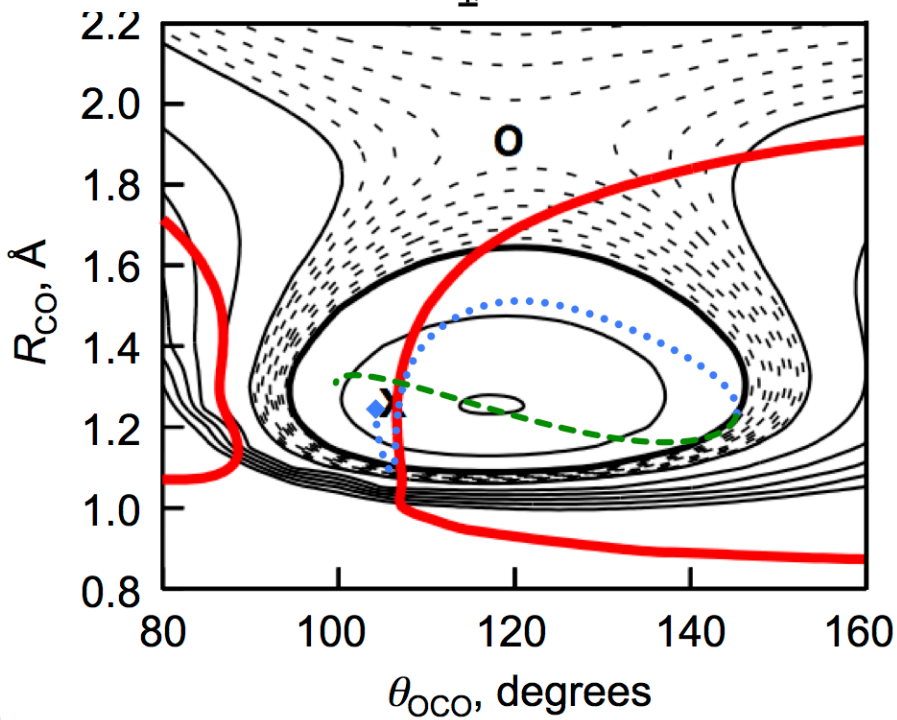
Two types of low-E_{perp} multidimensional probabilities

Two types of low E_{perp} multidimensional probabilities



LZ
IWC/2
1D CP
CP

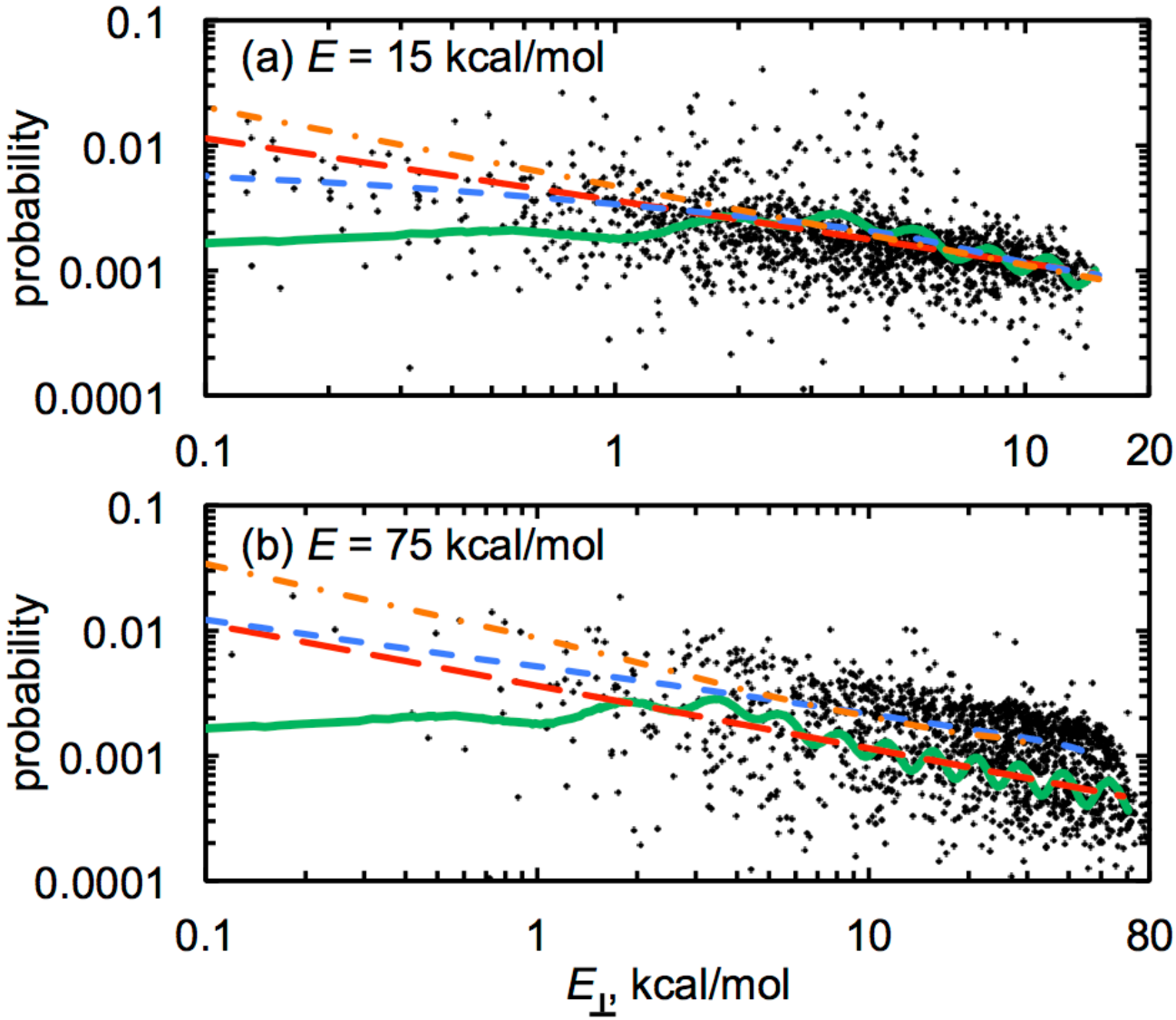
$\Delta t_{crossing}$ = small (few fs)
"prompt return" => similar to 1D
=> "weak coupling" limit



$\Delta t_{crossing}$ = larger (10s of fs)
"surfing" the seam => adiabatic limit
Not possible in 1D!

Relative importance of the WC and adiabatic limits depends on *E*.

Multidimensional P_{hop}: Full ensemble for CO_2



Methods

Full-D CP

binned & averaged

=> MD $P_{hop}(E,E_{perp})$

1D LZ

Full-D LZ

1D CP

Results

At low E & high E_{perp}

all methods agree

At low E & low E_{perp}

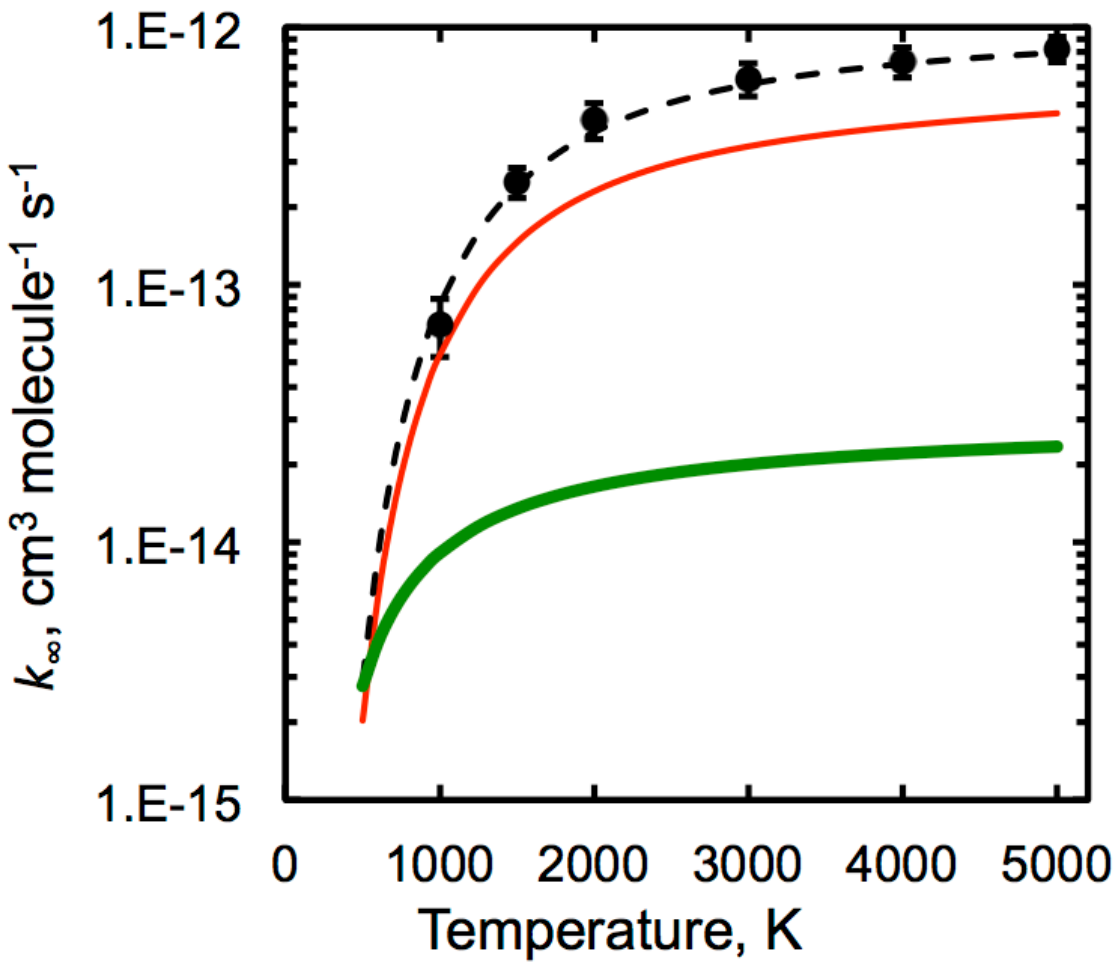
non-negligible nonlocal and dynamical MD effects

At higher E

non-negligible static MD effects (factor of 2)

High pressure limit

$^3O + CO \rightsquigarrow CO_2$



CSDM = (classical) MD P_{hop}

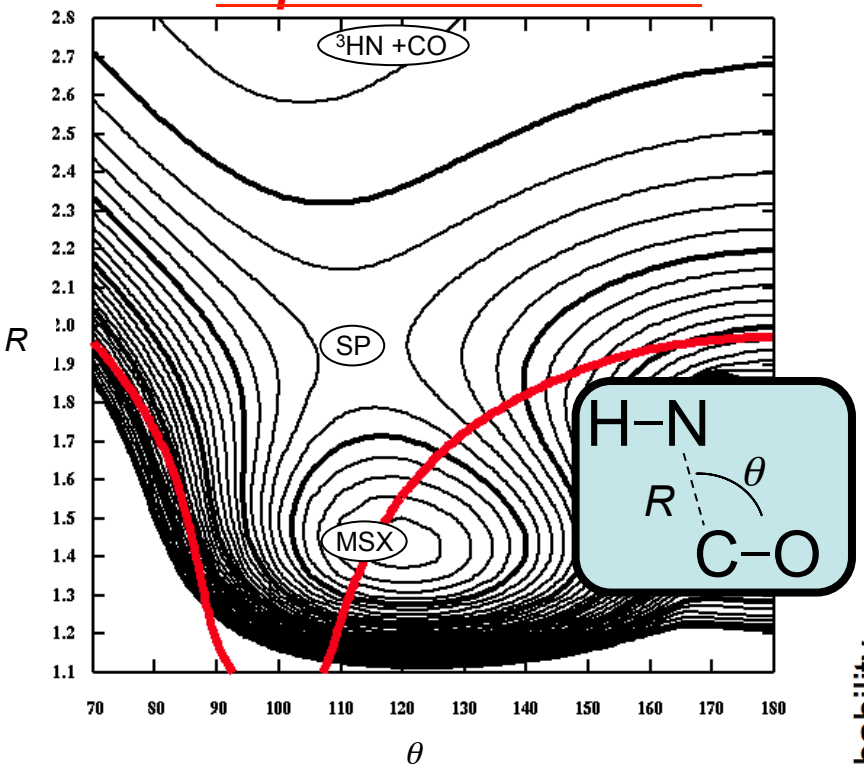
NA TST (1D LZ)

Estimate in many combustion models (1975)

Multidimensional P_{hop} for larger systems: HNCO

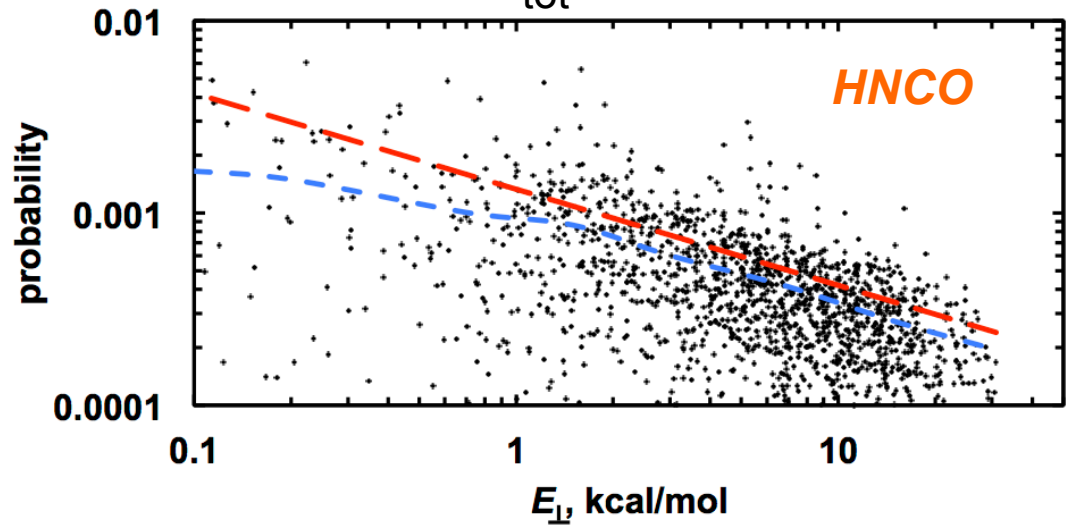
^{3}HNCO –> ^{3}HN+CO
~> ^{1}HNCO
(–> products)

Triplet HNCO surface

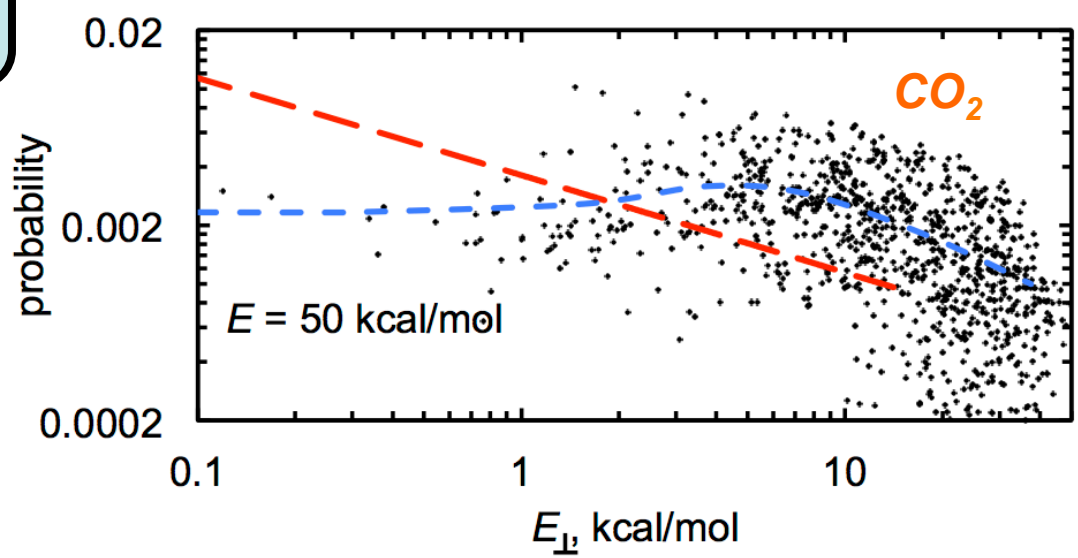


Short time MD CP trajectories
τ_{deco} is again short
Direct dynamics (M06-2x/dz)
Fitted S/T SO surface

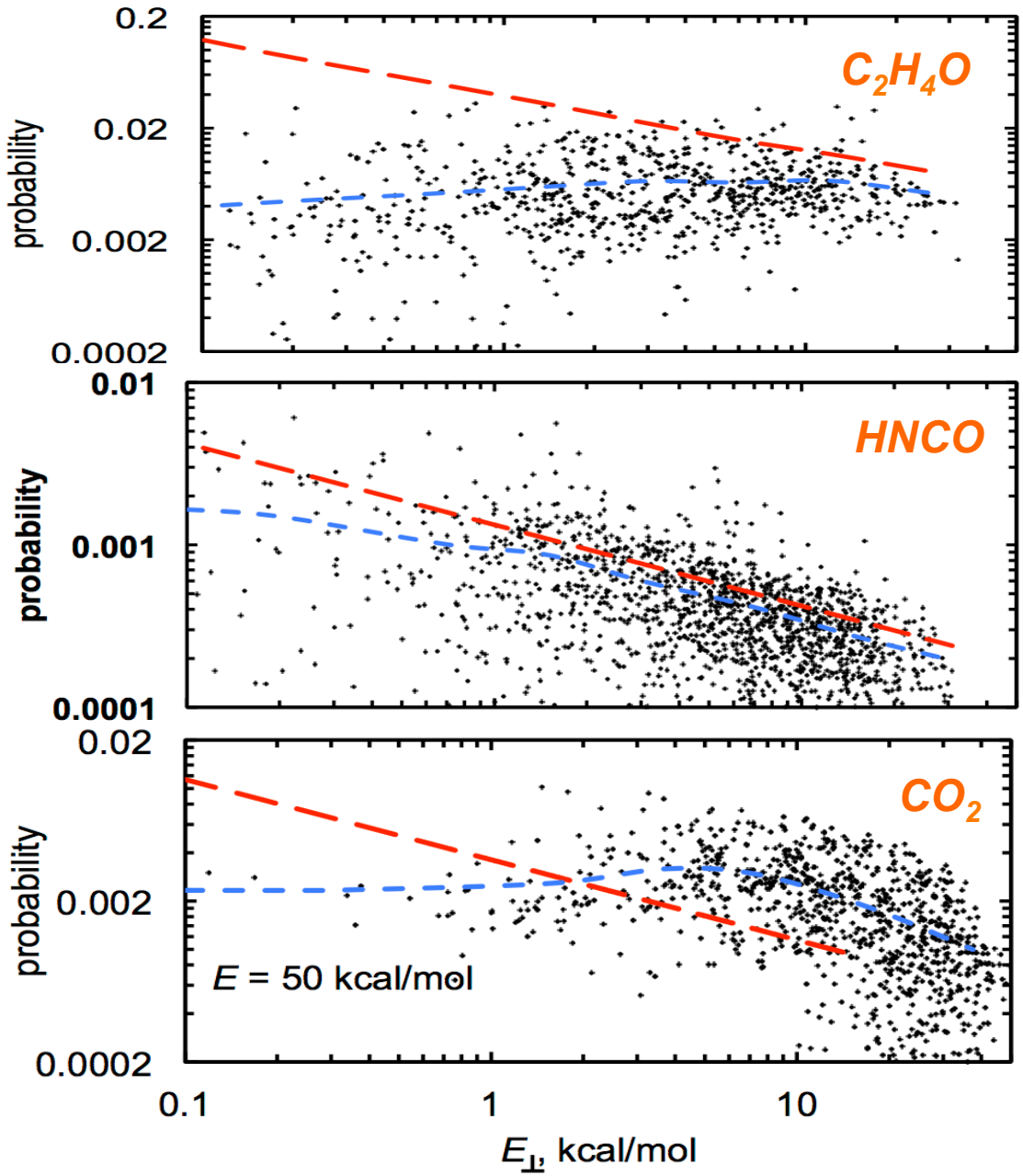
E_{tot} = 50 kcal/mol



Smaller MD effects for HNCO than for CO_2
Smaller E per DoF!



Multidimensional P_{hop} for CH_2CH_2O



$^3C_2H_4O$ –> ^3O + C_2H_4
~> $^1C_2H_4O$

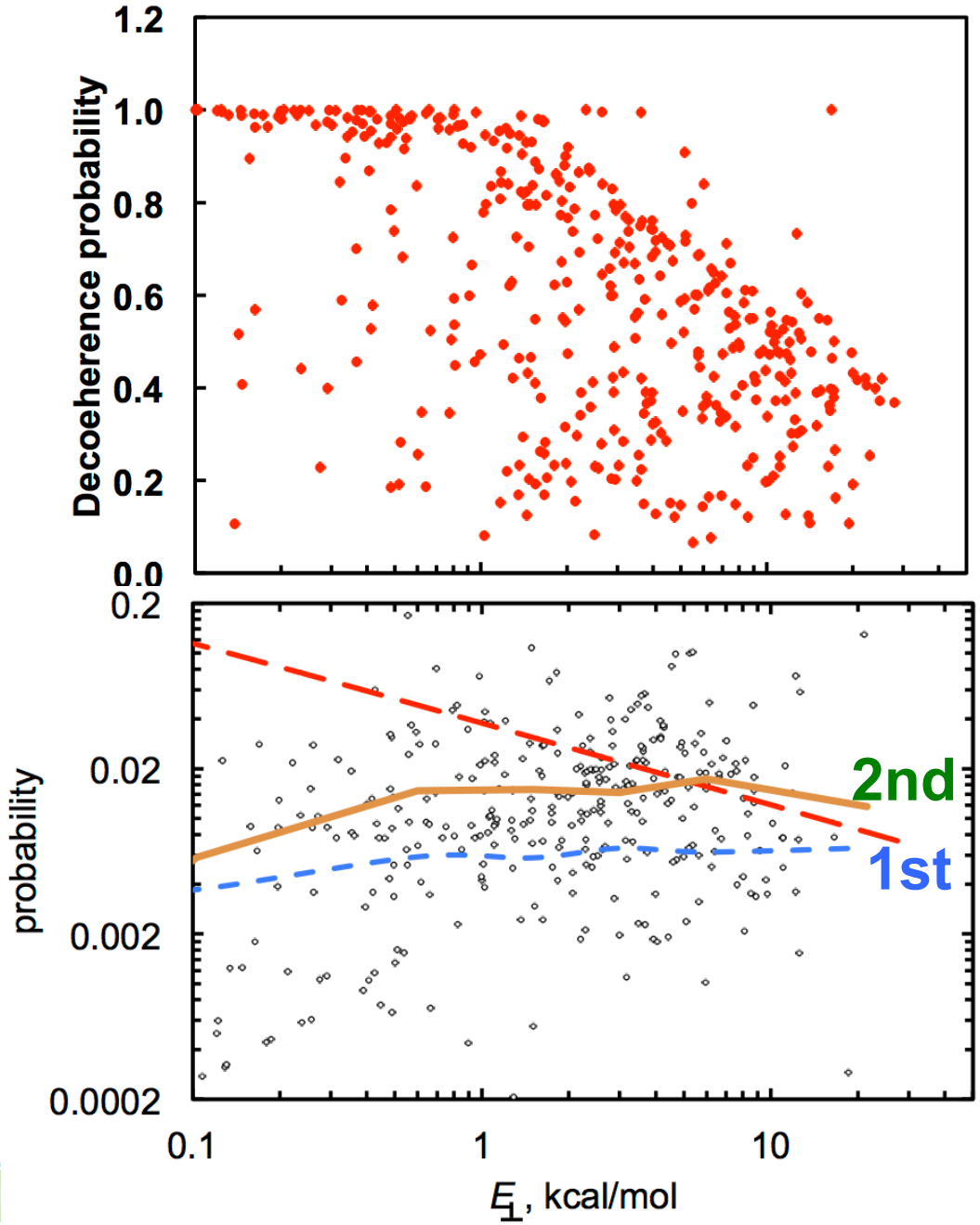
M06-2x/dz direct dynamics
Constant SO coupling

More DOF = more sensitive to low E_{perp}

Larger MD effects at low E

The S/T seam is "flatter" than for the other systems
→ phase interference
→ longer τ_{deco}

Electronic coherence in P_{hop} for CH_2CH_2O



$P_{deco} = 1\text{-}\exp(-\Delta t_X/\tau_{deco})$

τ_{deco} from a semiclassical model based on 1D wave packet overlaps

$P_{deco} = 1$ for CO_2 & HNCO

(De)coherence affects the electronic dynamics at the 2nd (and later) passages

Coherent dynamics is readily incorporated via the "short time" CP trajectories

Summary

Accurate gas phase theories of spin-forbidden kinetics aid in the development of combustion models

Full-dimensional CSDM trajectories

"De-mixing" is a semiclassical model for decoherence

Multidimensional nonadiabatic statistical theory

Static, dynamical, & nonlocal **multidimensional** effects

Decoherence (often) localizes nonadiabatic dynamics

MD P_{hop} from swarms of short-time trajectories & the classical path electronic TDSE

$US DOE BES