Theoretical methods for combustion kinetics: Collisional energy transfer and spin-forbidden chemistry

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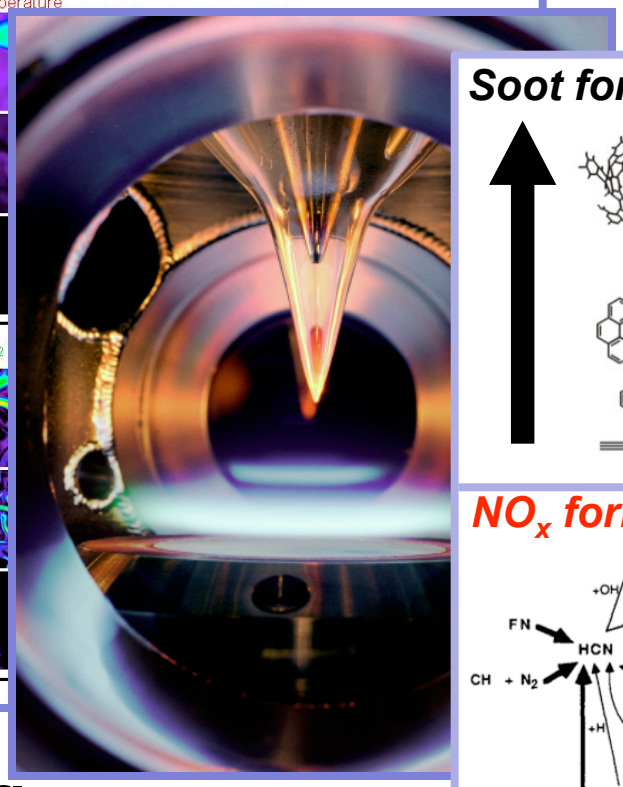
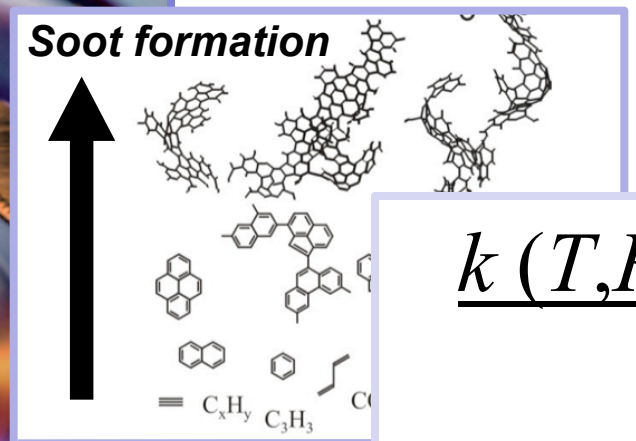
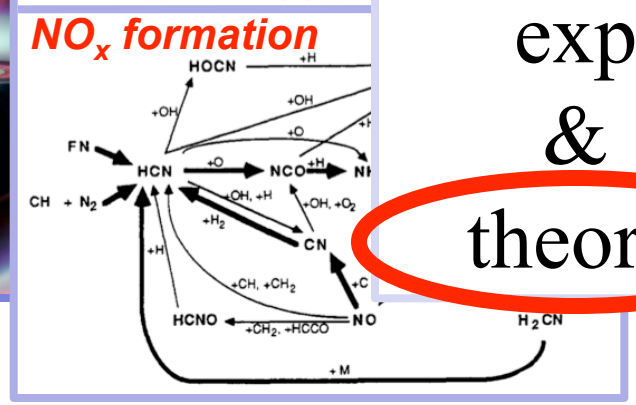






$k\,(T,P)$

exp
&
theory

Engines

Reacting flows

Model flames

Chemistry

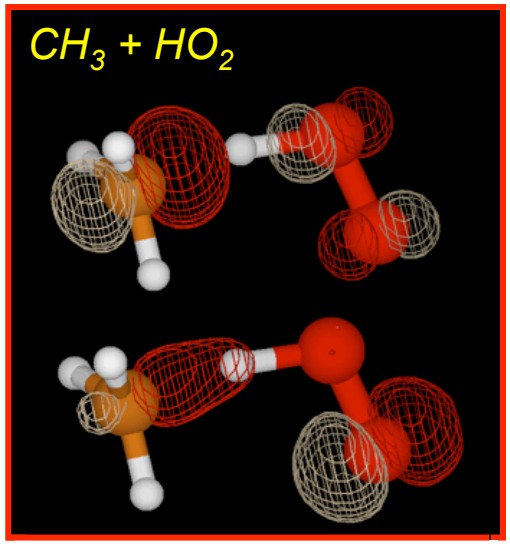
Kinetics

$ DOE OBES

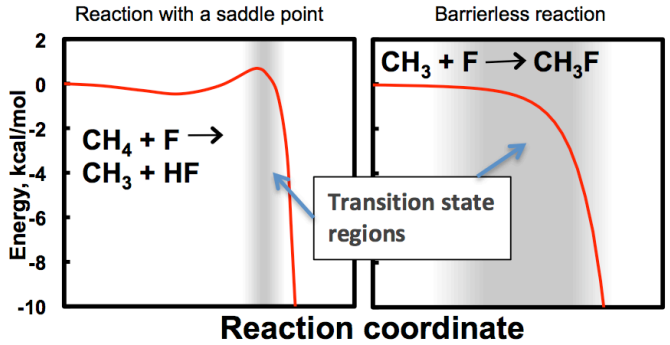
Theoretical Chemical Kinetics

Introduction: Methods

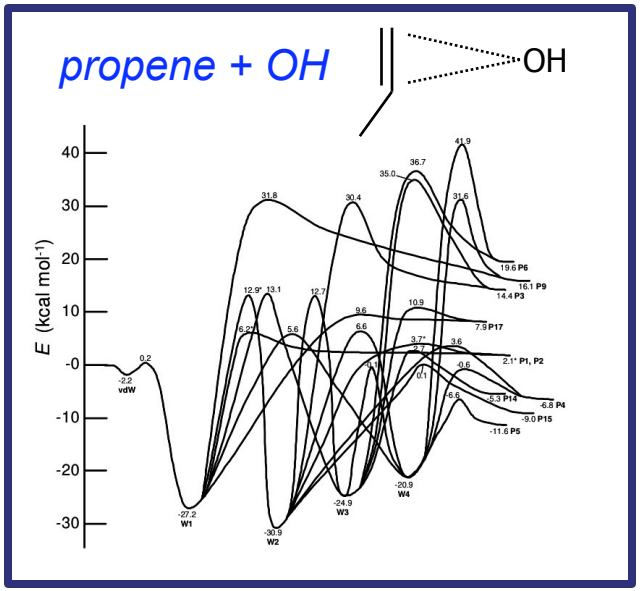
Quantum chemistry



Transition state theory



Master equation analysis



Geometries

Frequencies

Barrier heights

Reaction enthalpies

uncertainty →

Elementary kinetics

k(E) ± ?

uncertainty →

Phenomenological rate coefficients

k(T,P) ± ?

Theoretical Chemical Kinetics

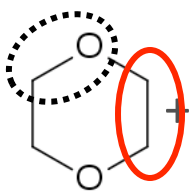
Recent application 1: Dioxane

Ring opening reactions: dioxane, cycloalkanes

Rings found in "new" fuels: tars, biofuels

Opening rate & mechanism affect oxidation

exp: Rob Tranter, Argonne, shock tube



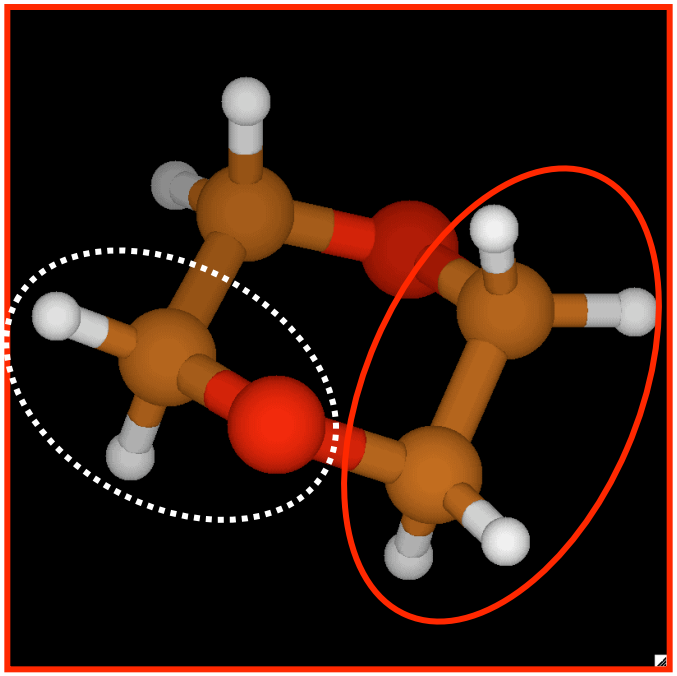
+ heat →

m/z = 30 (CH_2O)

28 (C_2H_4/CO)

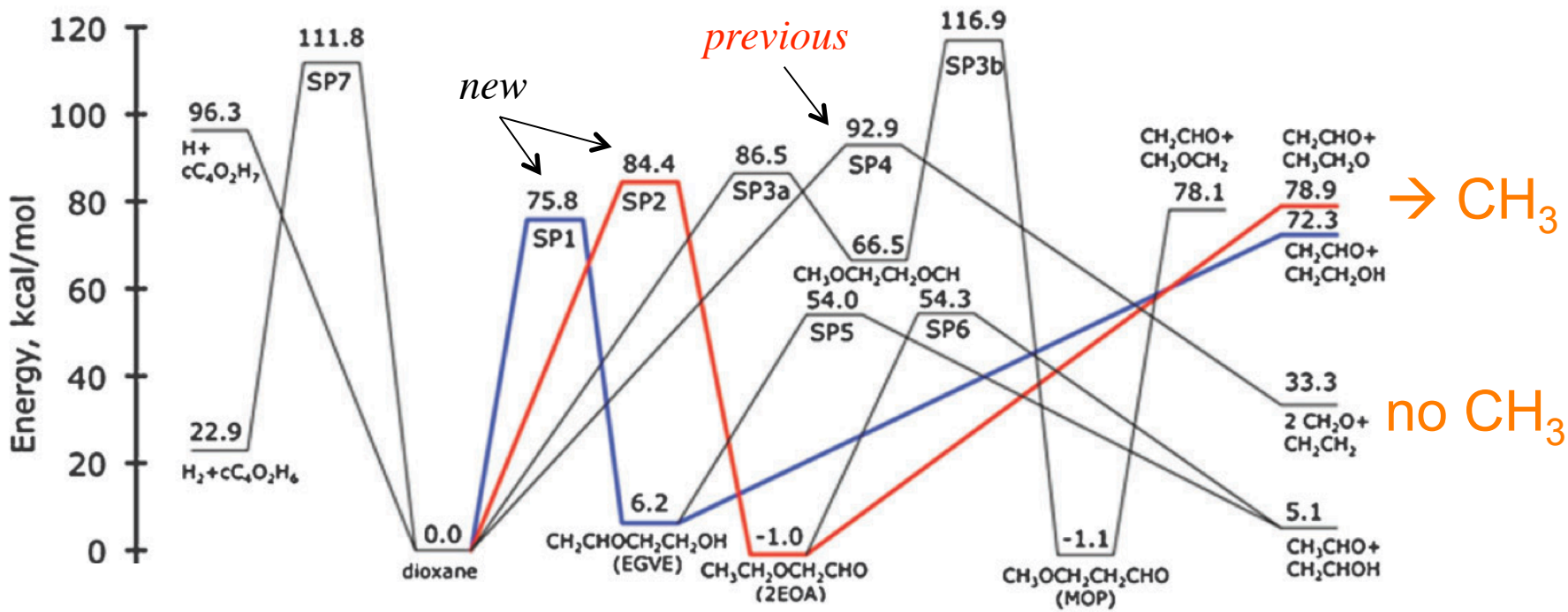
15 (CH_3)

} observed



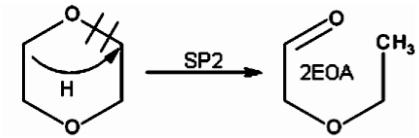
Dioxane ring opening

q.c. method: **QCISD(T)/CBS//B3LYP/6-311++G(d,p)**
with **MRCI+Q//CASPT2** for some geometries



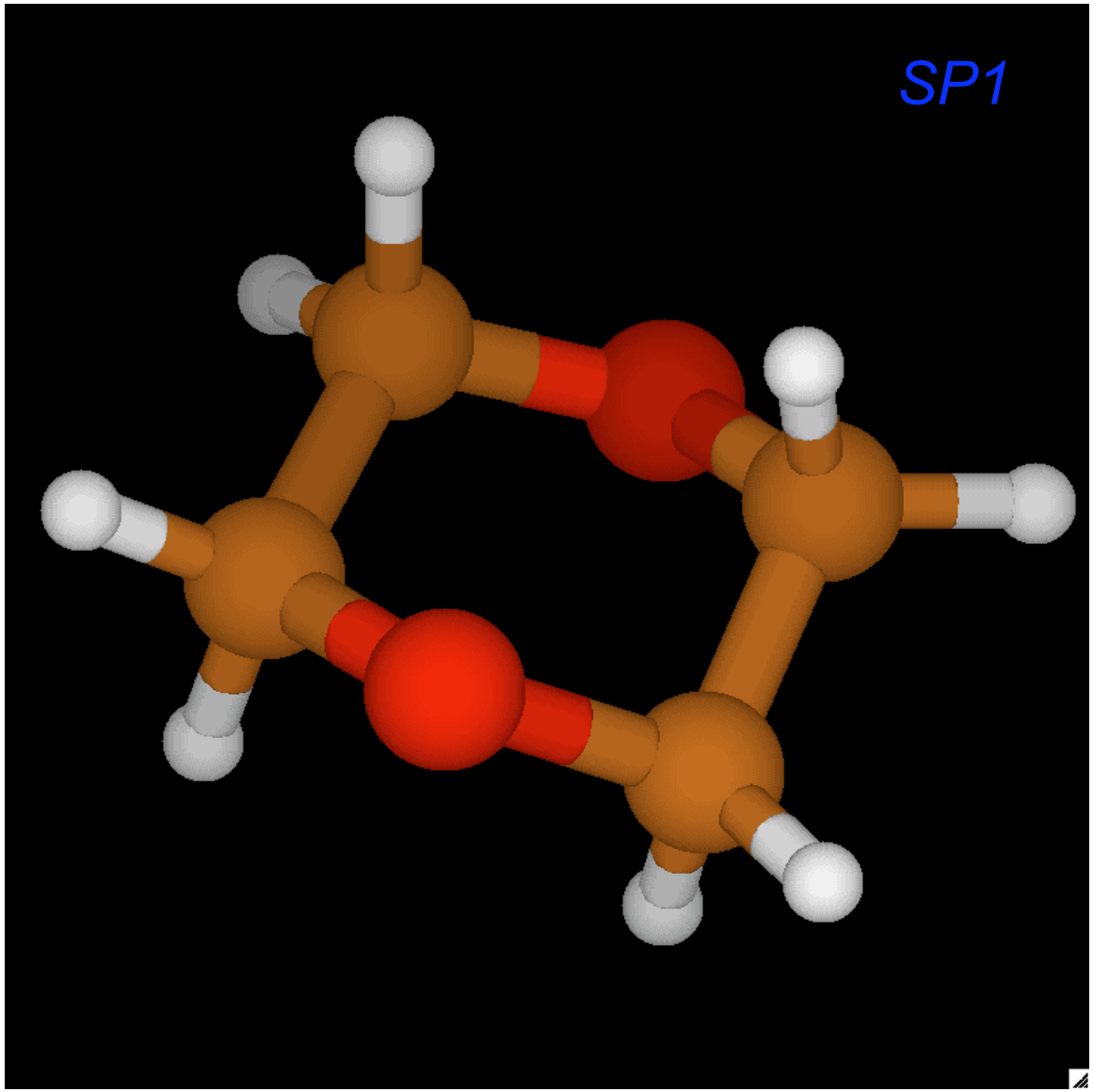
blue

red



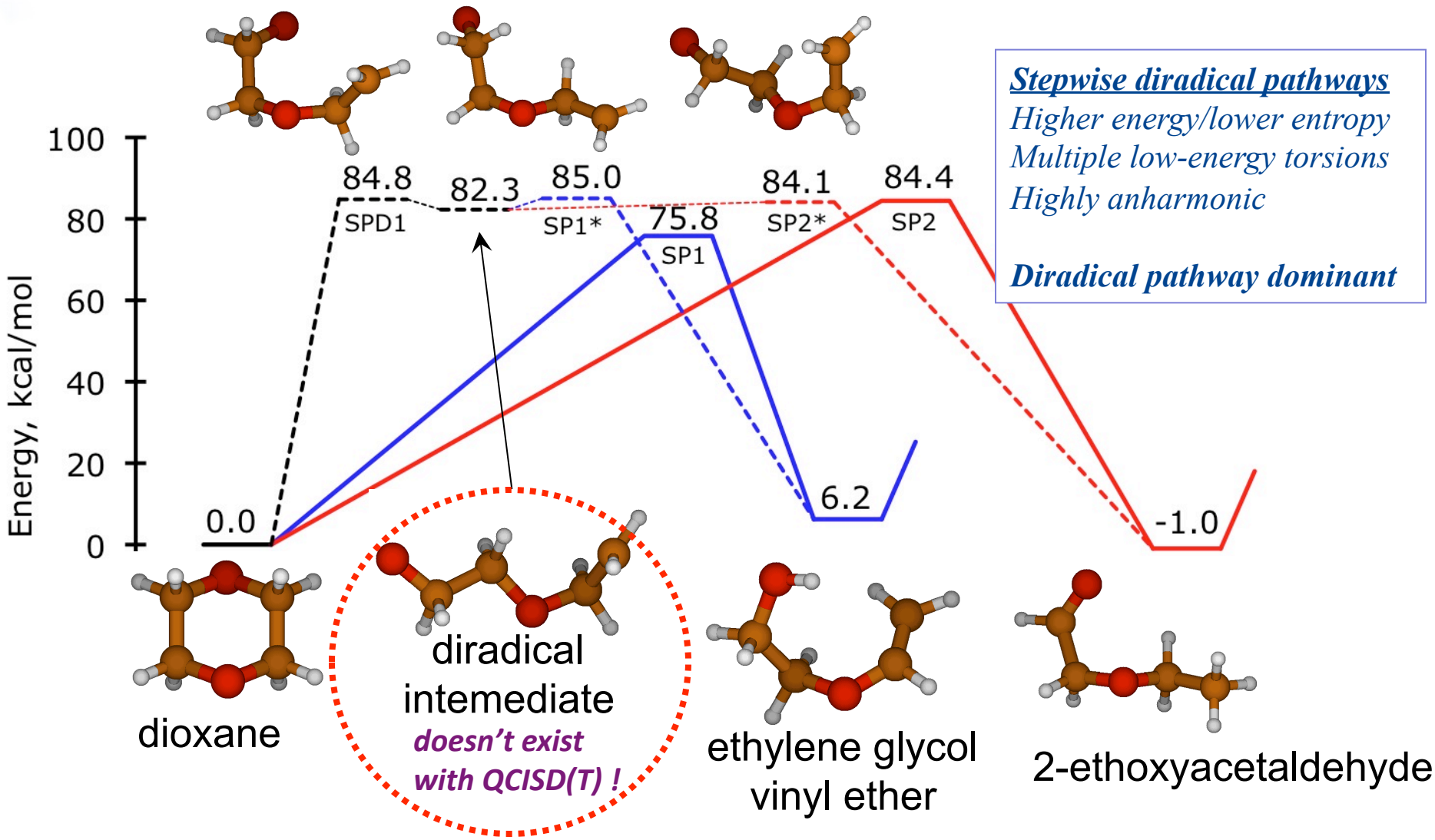
Theoretical Chemical Kinetics

Concerted IRC



Concerted vs stepwise mechanisms

For every concerted mechanism, one can always find stepwise analogs



Stepwise diradical pathways

Higher energy/lower entropy

Multiple low-energy torsions

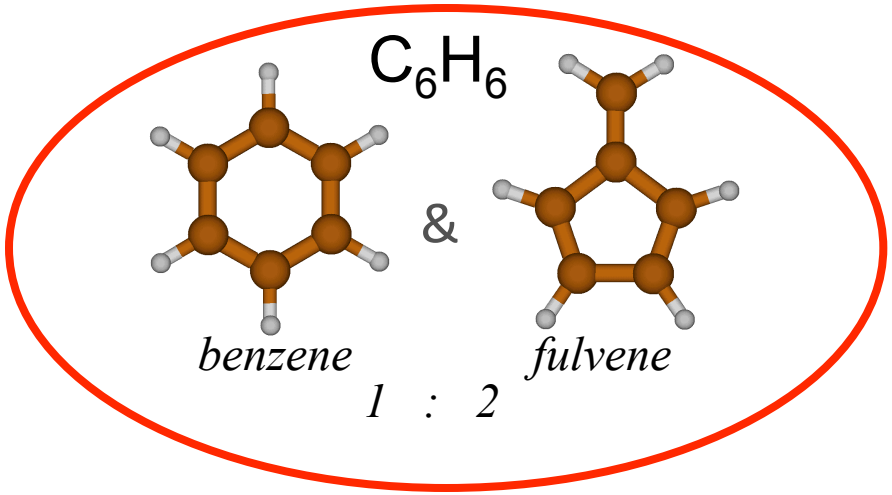
Highly anharmonic

Diradical pathway dominant

Theoretical Chemical Kinetics

Recent application 2: H assisted isomerization

How does fuel structure affect benzene formation?



- Benzene leads to PAHs & soot
- Known rates & branching for major formation channels

  $C_4H_5 + C_2H_2 \rightarrow C_6H_6 + H$

  $C_3H_3 + C_3H_3 \rightarrow C_6H_6$

- Hansen (Sandia), flame experiments

  Plots [benzene] vs [precursors]

  Correlation suggests mechanism

  [benzene] > [fulvene]

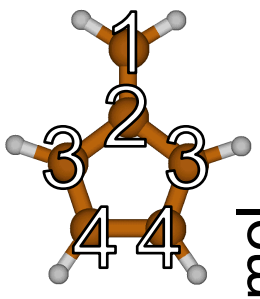
Where is the fulvene going?

Theoretical Chemical Kinetics

Recent application 2: H assisted isomerization

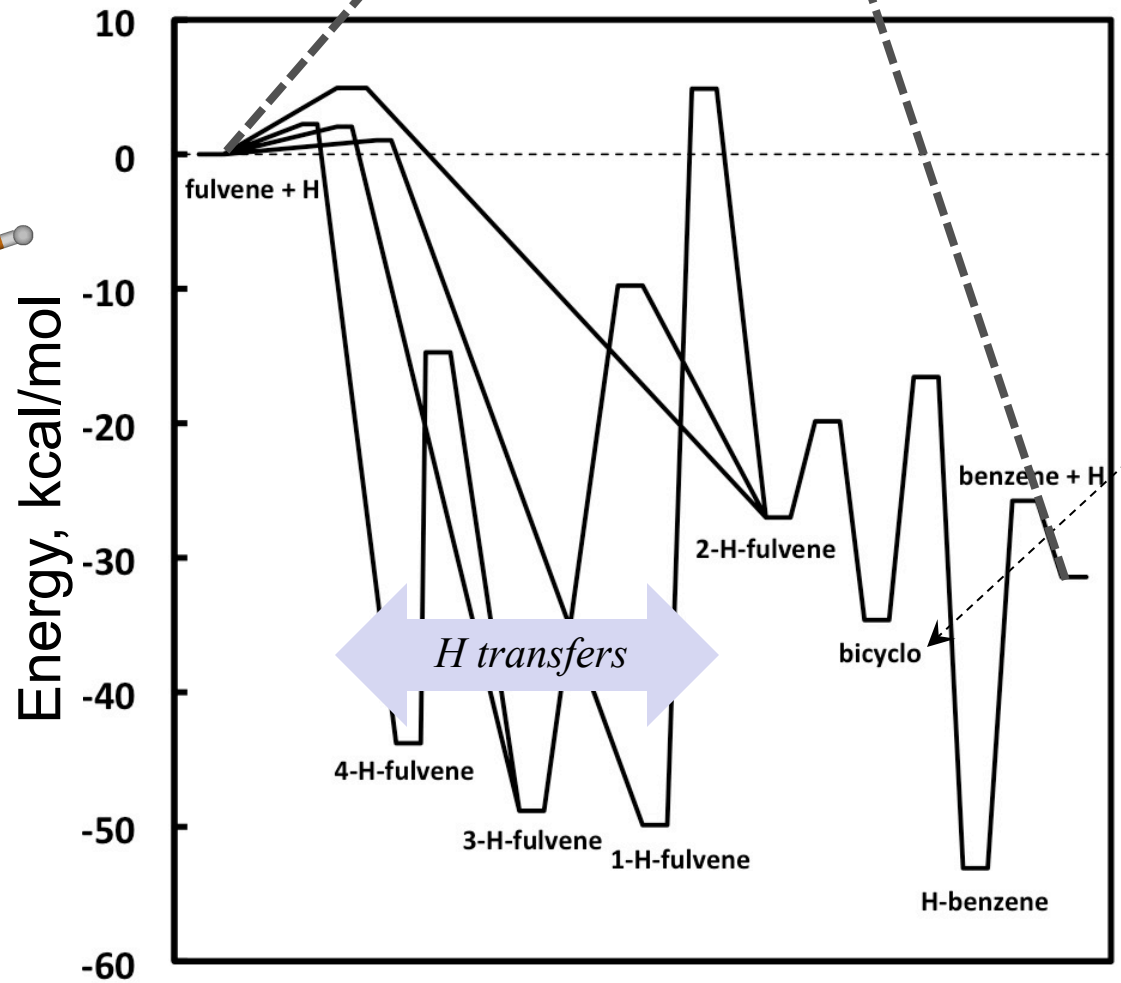
Plenty of H radicals in flames

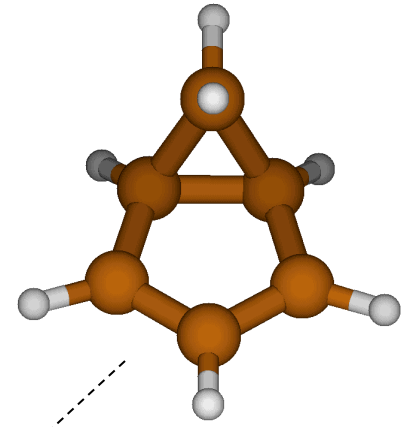
+75 kcal/mol -- Bicyclo saddle point w/o H



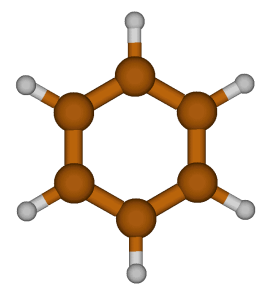
+

H





H stabilizes this bicylo intermediate

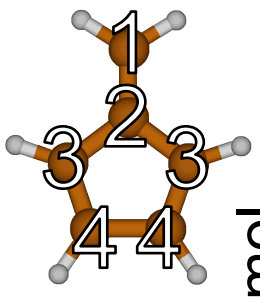


+ H

Theoretical Chemical Kinetics

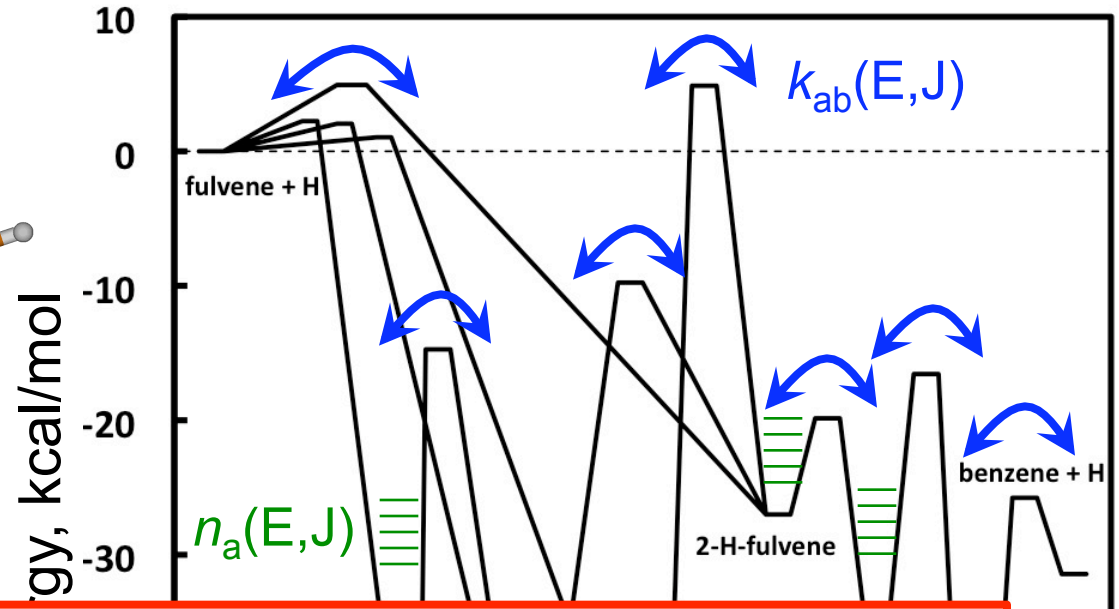
Recent application 2: H assisted isomerization

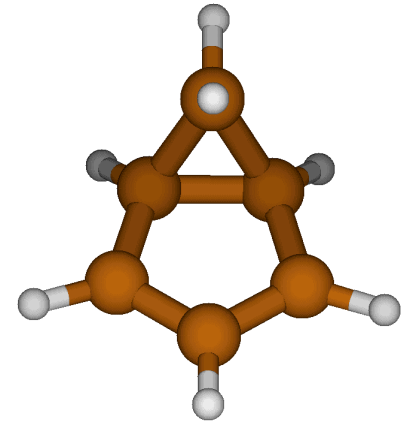
Plenty of H radicals in flames



+

H





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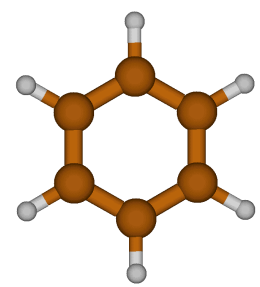


+ H

Master equation

$$\frac{dn_a(E,J)}{dt} = \sum_{b\neq a} k_{b,a}(E,J)n_b(E,J)$$

IN from reactants, other wells

$$-\sum_{b\neq a} k_{a,b}(E,J)n_a(E,J)$$

OUT to products, reactants, other wells

bath gas collisions IN & OUT

$$+ Z(T)\sum_{J'}\int_{E'} P(E,J \leftarrow E',J')n_a(E',J')dE' - Z(T)n_a(E,J)$$

Typically empirical

Theoretical Chemical Kinetics

What's missing?

Predictive models for collisional energy transfer

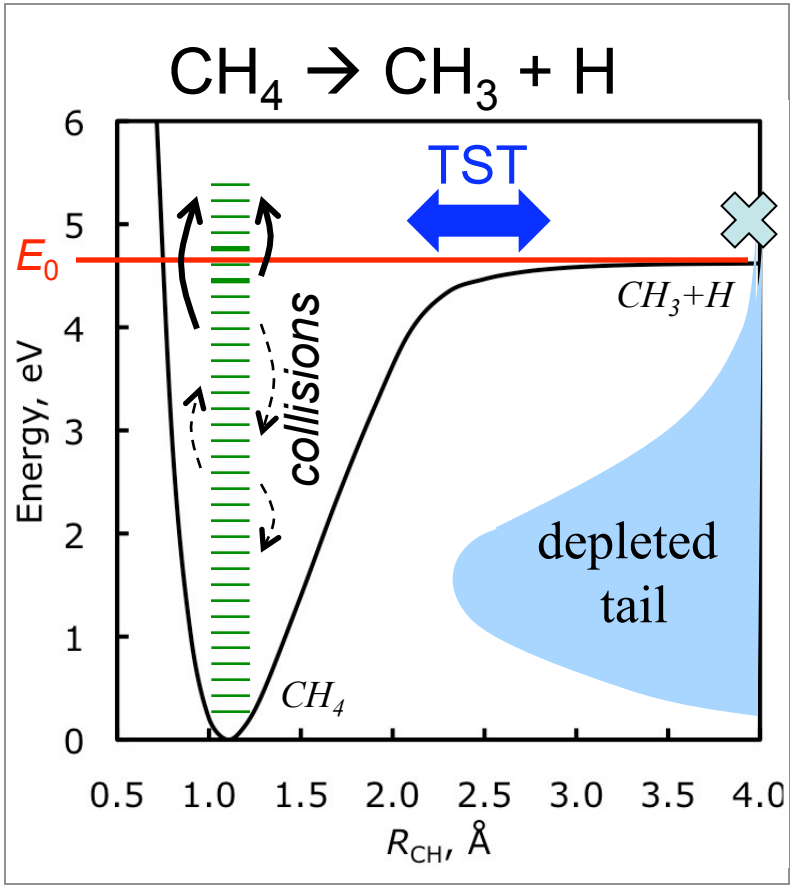
- Collisions stabilize intermediates at rates that can compete with intramolecular processes
- In the high pressure limit

  $k_{TST} << k_{collisions}$

  The TS is rate limiting
- In the low pressure limit

  $k_{TST} >> k_{collisions}$

  Threshold collisions are rate limiting
- Competition at intermediate pressures
- $k_{collision}$ is almost always treated as an empricial parameter



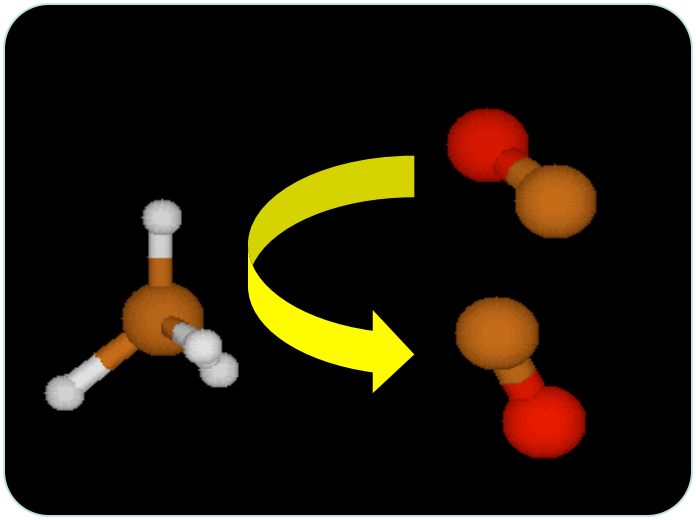
Collisional energy transfer

"Single exponential down" model

$$\text{rate of } E \rightarrow E' \text{ events} \propto Z\ e^{-(E'-E)/\alpha}$$

collision rate

assumptions:
distribution of *E'* is exp
independent of *J*
independnet of *E*



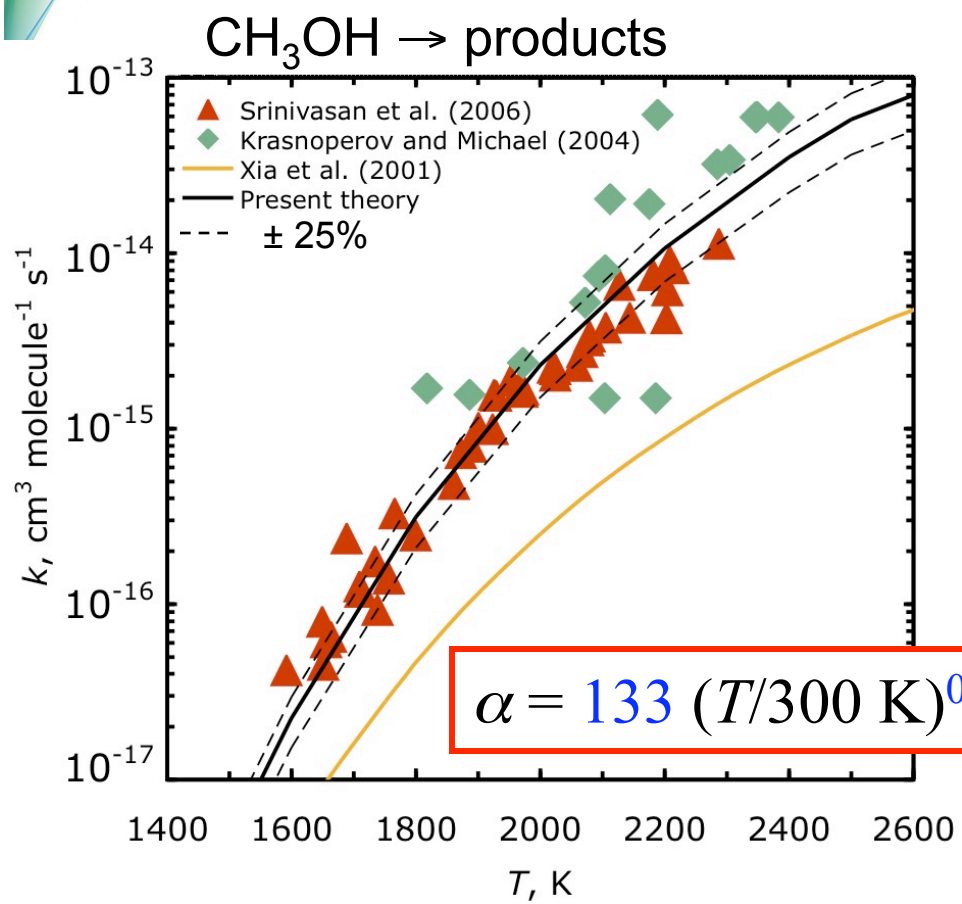
The "width" parameter is

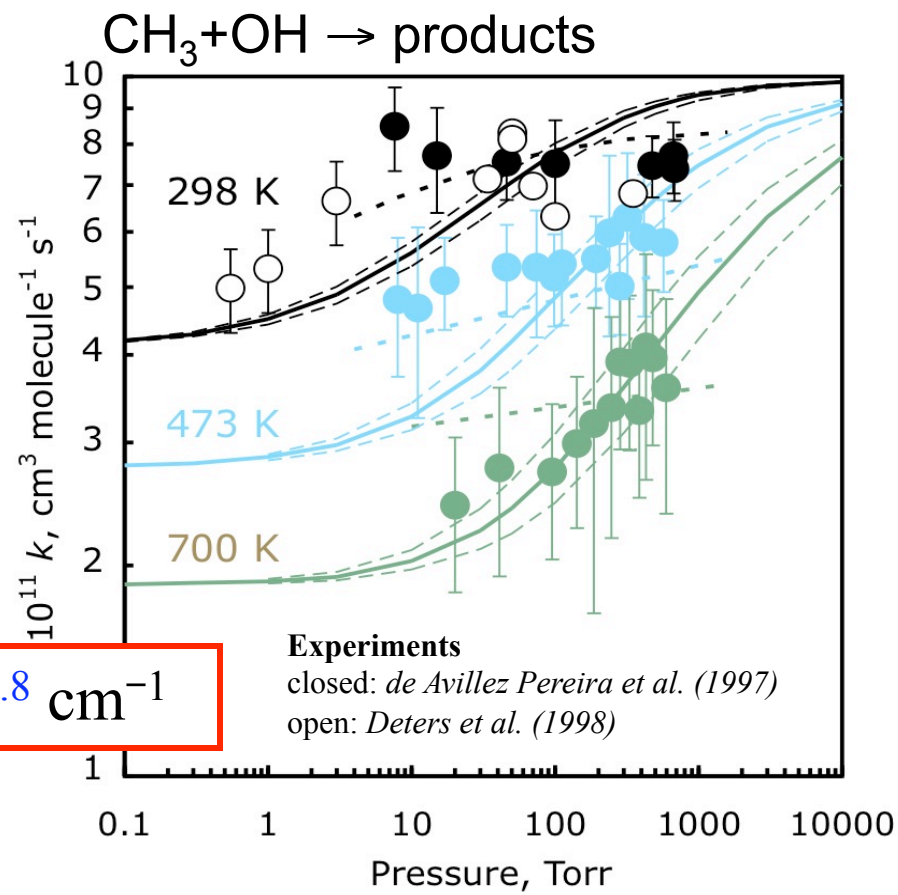
$$\alpha = < \Delta E_d >$$ = the average ΔE in deactivating collisions

$$= \alpha_{300}(T/300K)^n$$

Typically ***empirically*** determined

Empirical energy transfer parameters





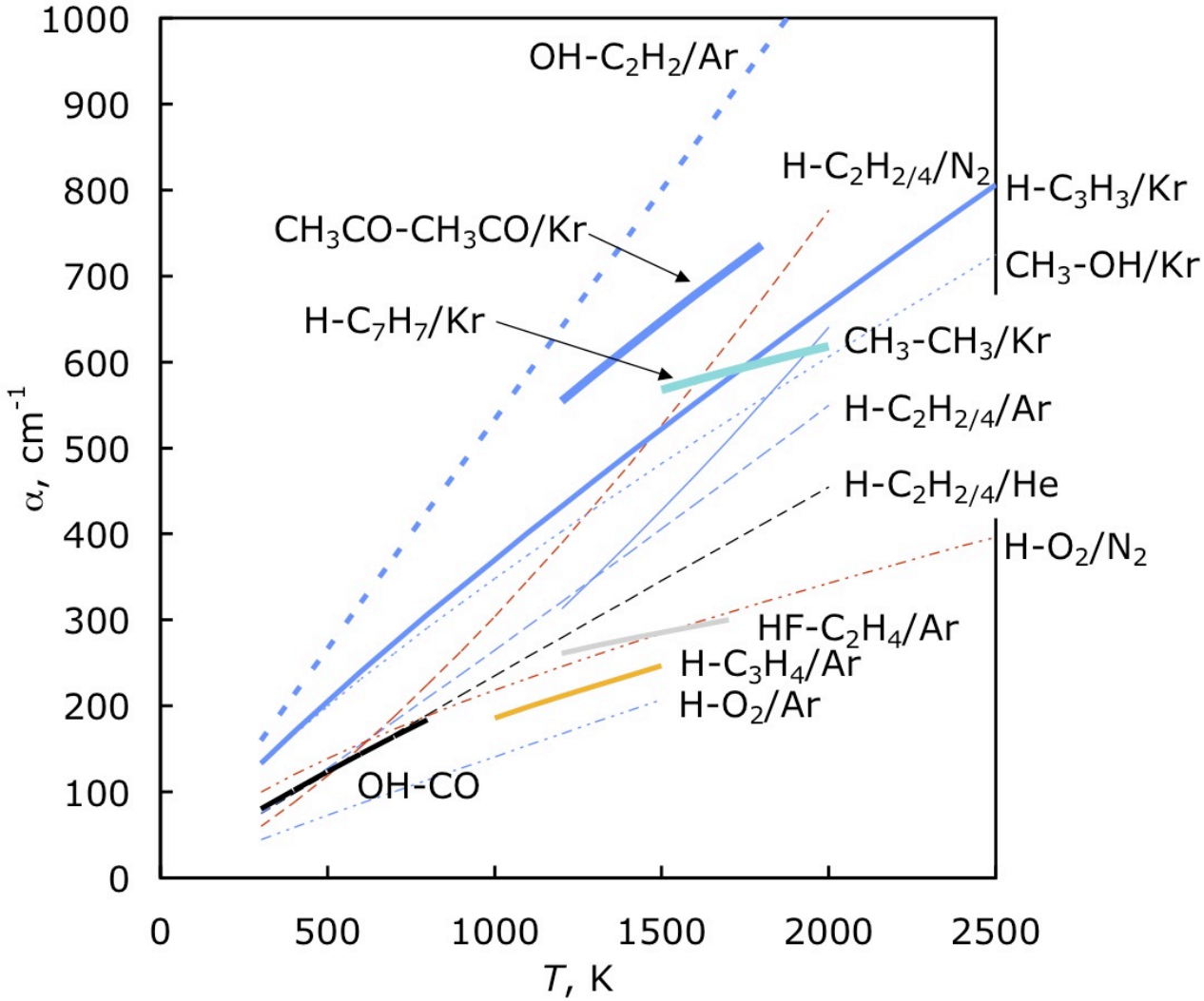
$$\alpha = 133\ (T/300\ \mathrm{K})^{0.8}\ \mathrm{cm}^{-1}$$

+ *Similar parameters work well for a variety of systems*

− *But not always*

Empirical energy transfer parameters

Survey

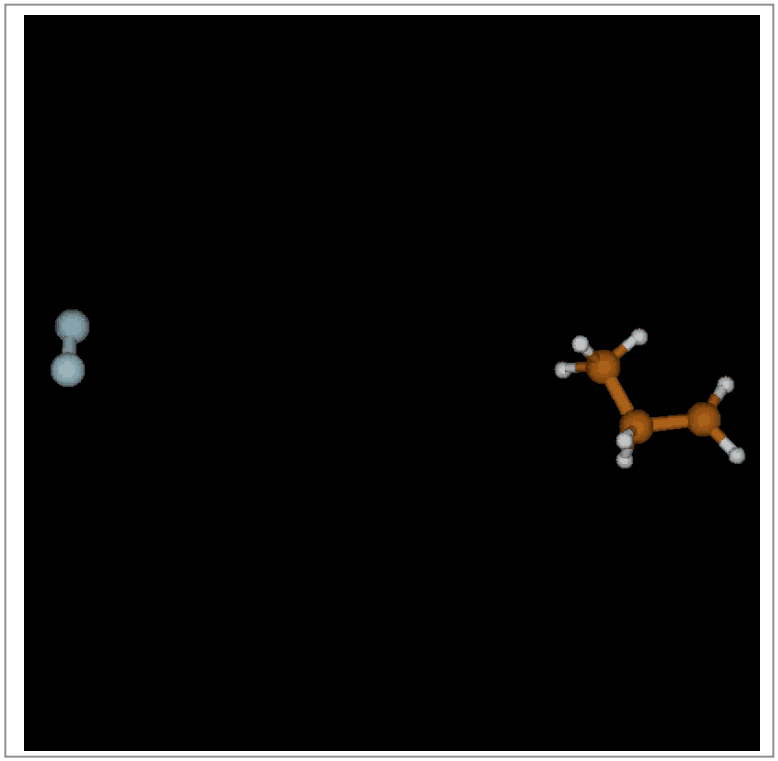


Literature

- Miller & Klippenstein ME formalism
- Fit to falloff data
- α_{fit} may be sensitive to D_0, Z, etc…
- Kinetics may be weakly dependent on α_{fit}

Predicting energy transfer with classical trajectories

n-propyl + N_2



Straightforward simulations

- Initial energy of the target ≈ E_0
- Thermal distributions for the bath, J
- Small ensembles of collisions (~1000)
- Calculate $\alpha(T) = \langle \Delta E_d \rangle (T)$ cm^{-1}

Accuracy determined by the interaction potential

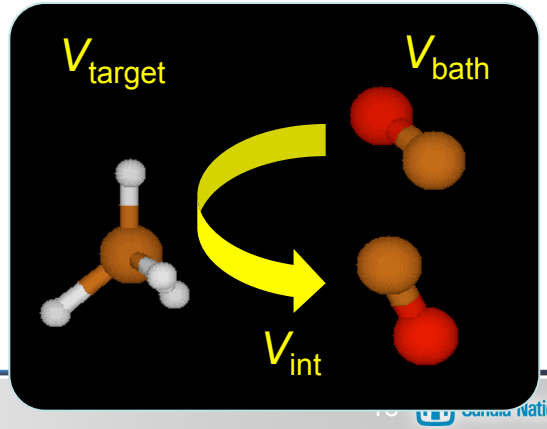
- Direct dynamics (MP2)
- Test more efficient PESs (Lennard-Jones, etc.)
- Developed cheap, accurate PESs for hydrocarbons in several baths

Separable pairwise approximation

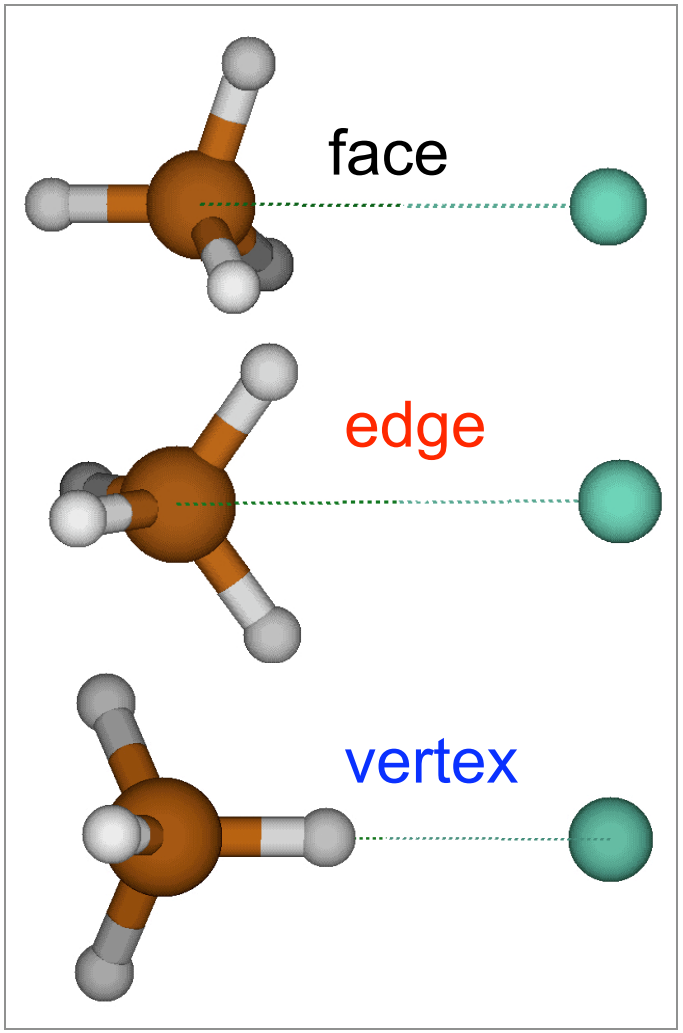
$V_{full} \approx V_{target}$ Cheap semiempirical method (TB)

$+ V_{bath}$ Exact for atomic & diatomic baths

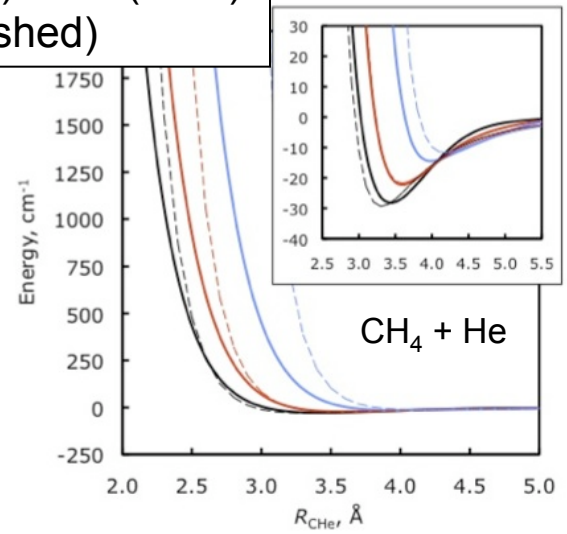
$+ V_{int}$ Buckingham (exp/6) interactions



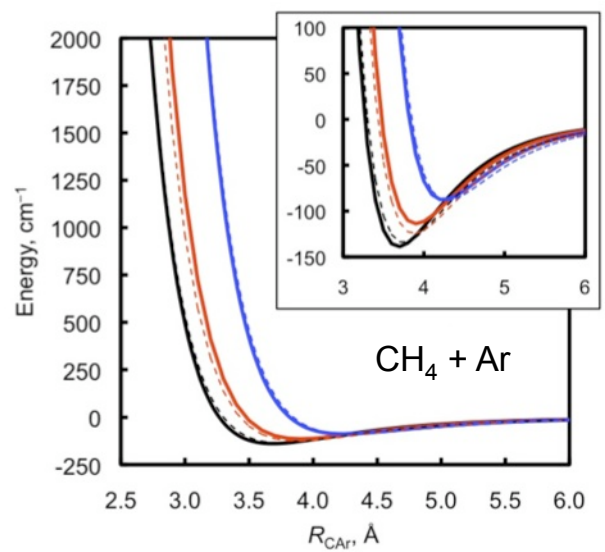
Accurate Interaction Potentials



QCISD(T)/CBS (solid)
fitted (dashed)

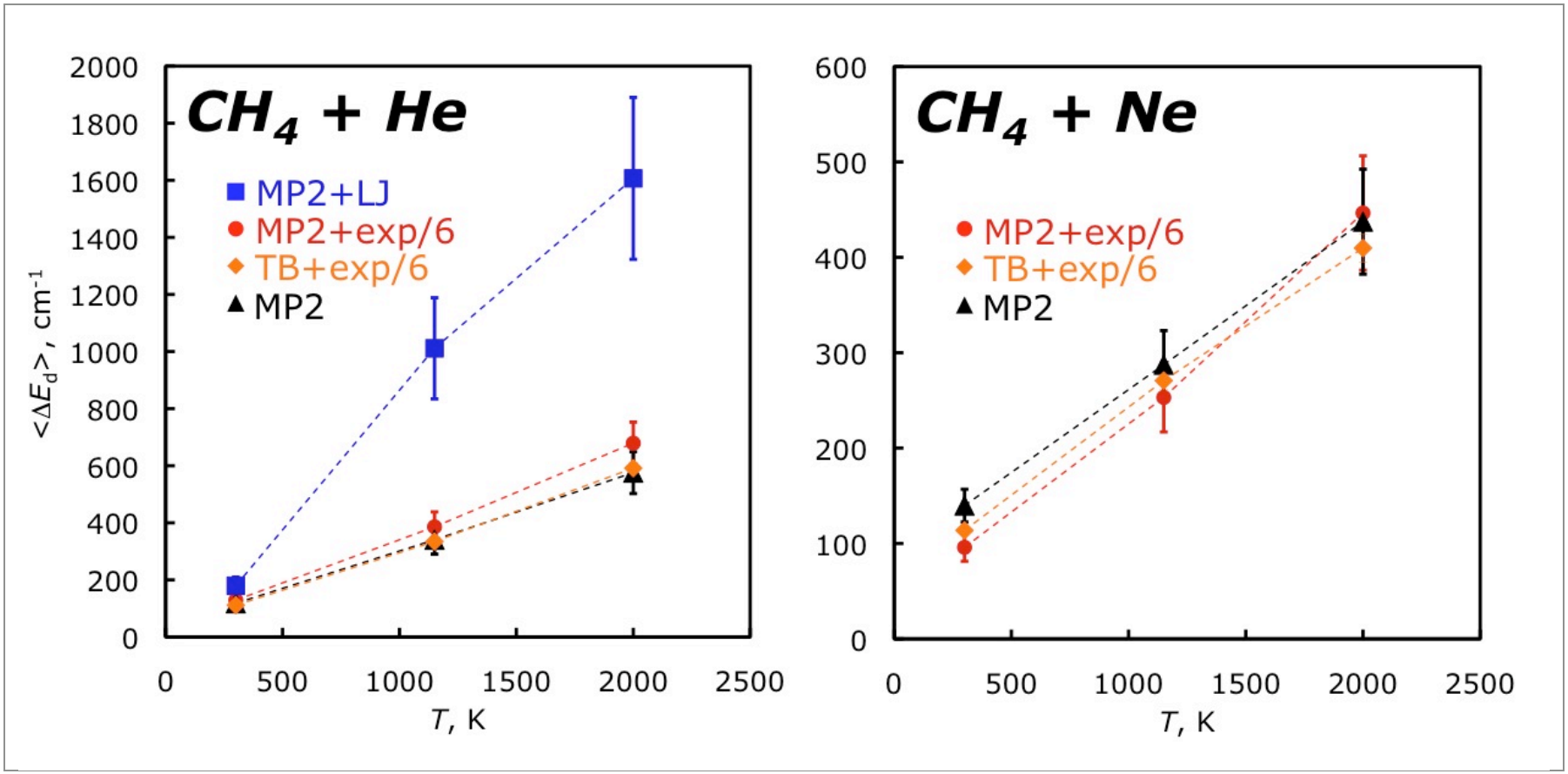


LJ (12/6)
Poor description of the repulsive wall



exp/6
Globally accurate for atomic baths

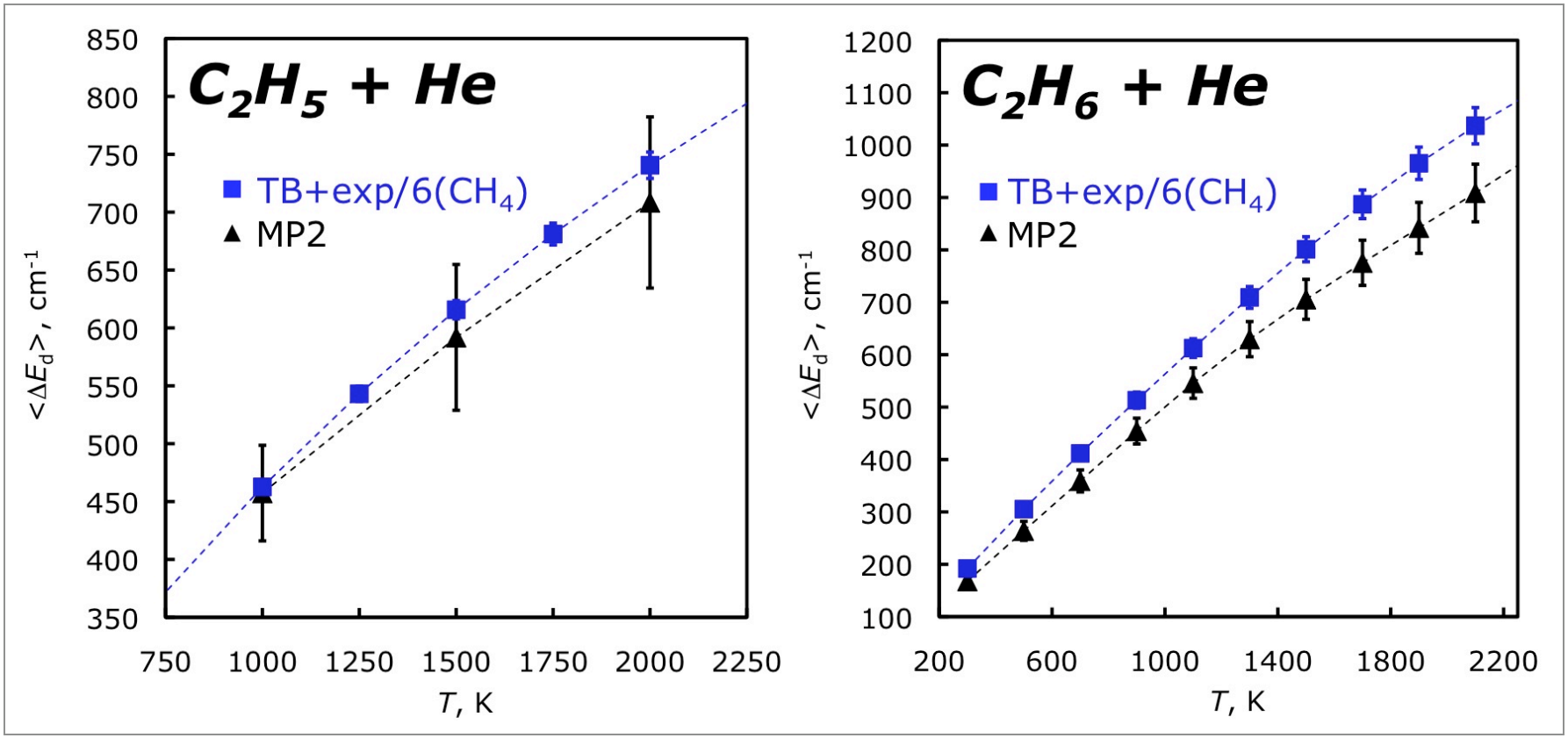
Tests of the separable pairwise method



- ✓LJ is confirmed to be inaccurate
- ✓MP2+exp/6 agrees with full direct MP2
- ✓TB: A cheap semiempirical description of the target works as well as MP2

TB+exp/6 is >1000x faster than MP2!

Test of "universal" exp/6 parameters



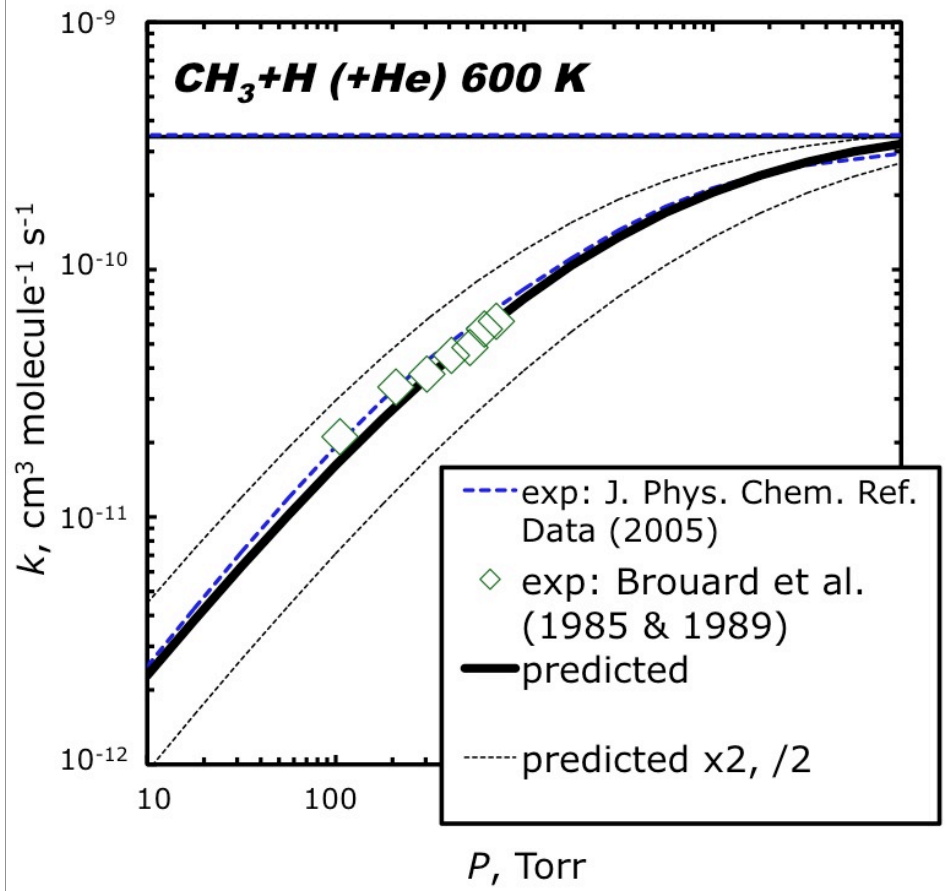
✓"Universal" exp/6 parameters have errors of 0-15%

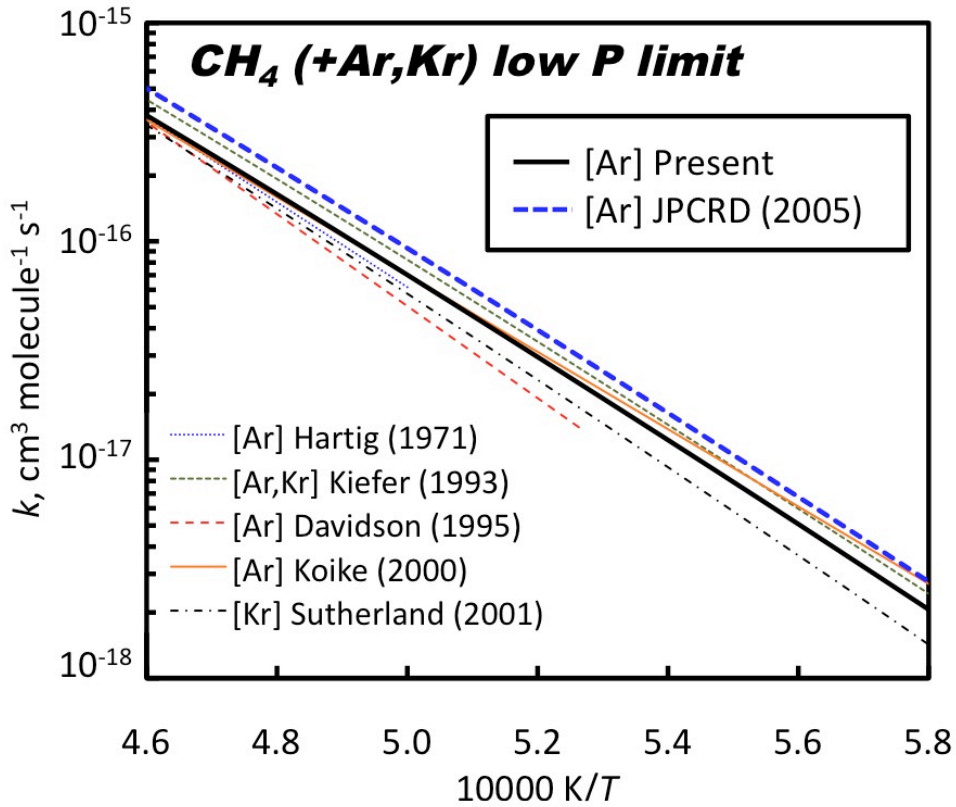
✓The TB approximation for the target is again quite accurate

✓The universal TB+exp/6 approach is readily applied to large systems

Accuracy of parameter-free kinetics

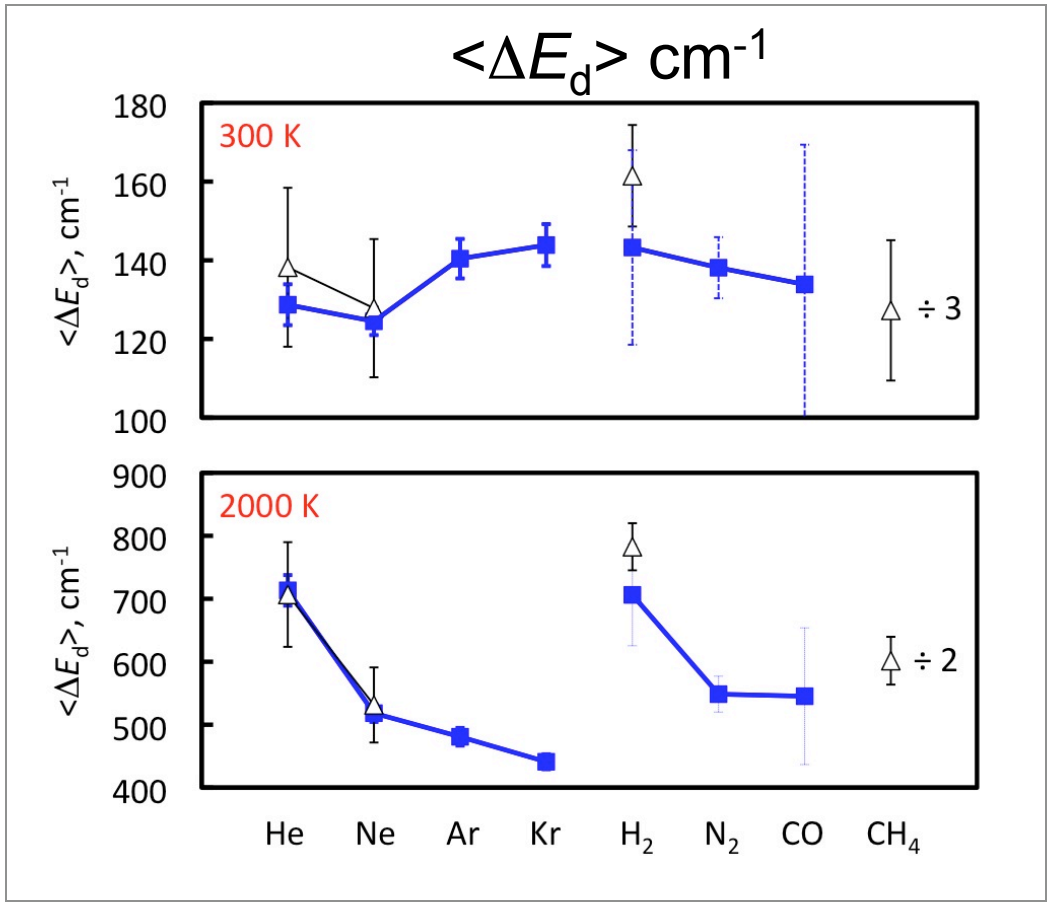
Test against low pressure & falloff measurements for CH_4 + M





Trends vs. the bath

CH_4 in eight baths (MP2 and TB+exp/6)



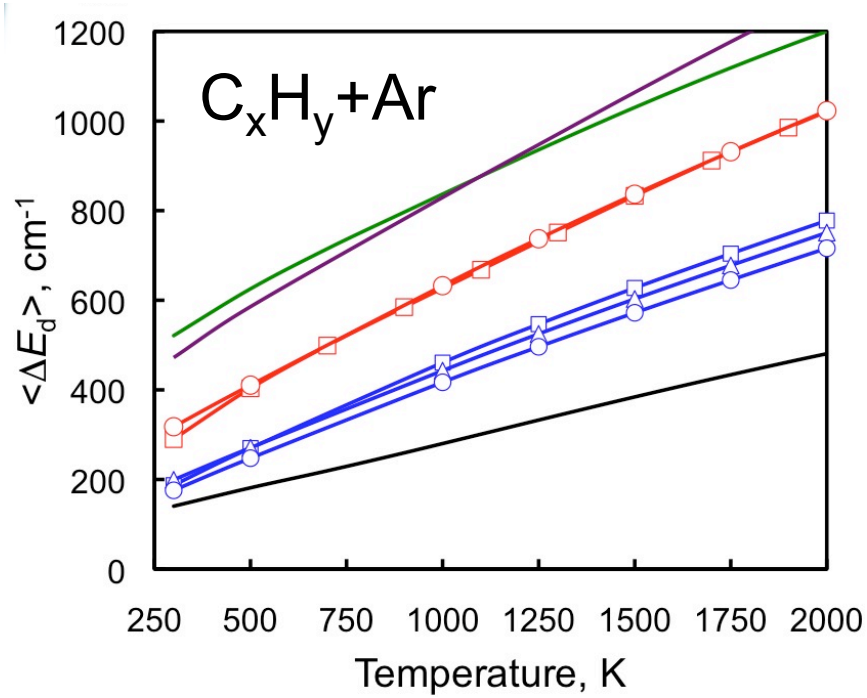
Controlled by vdw well

Controlled by mass, size

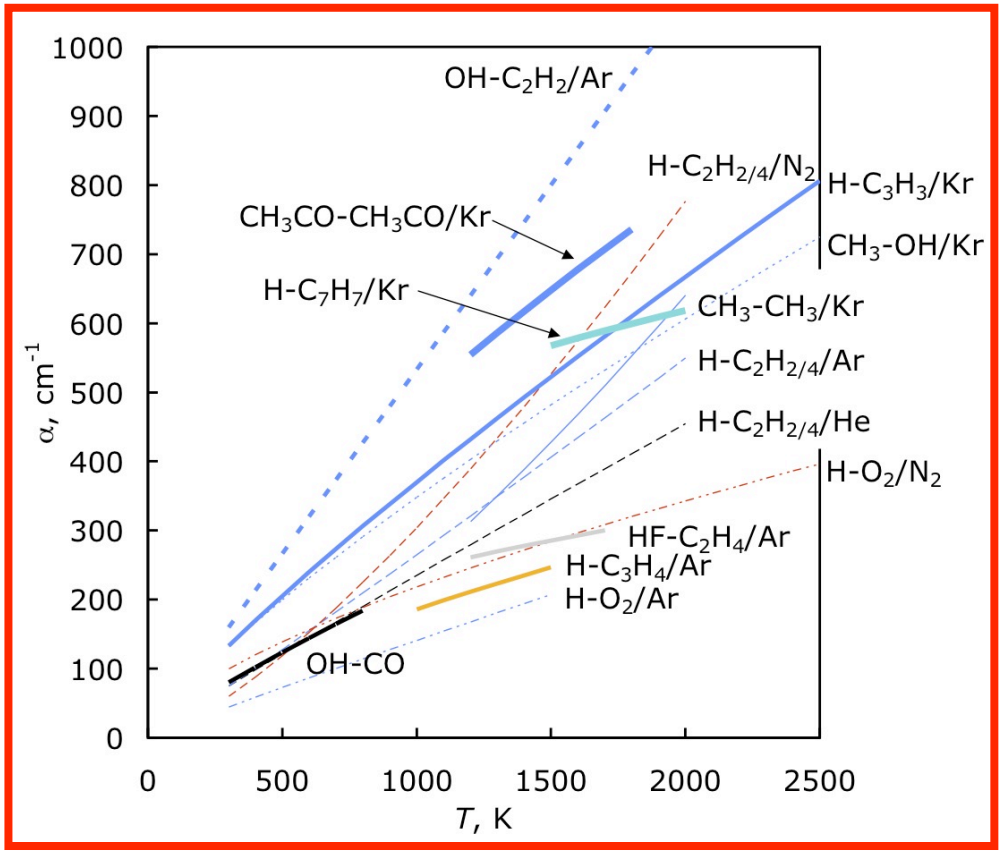
✓Relative efficiencies are temperature dependent

Trends vs. the target

Calculated



Empirical



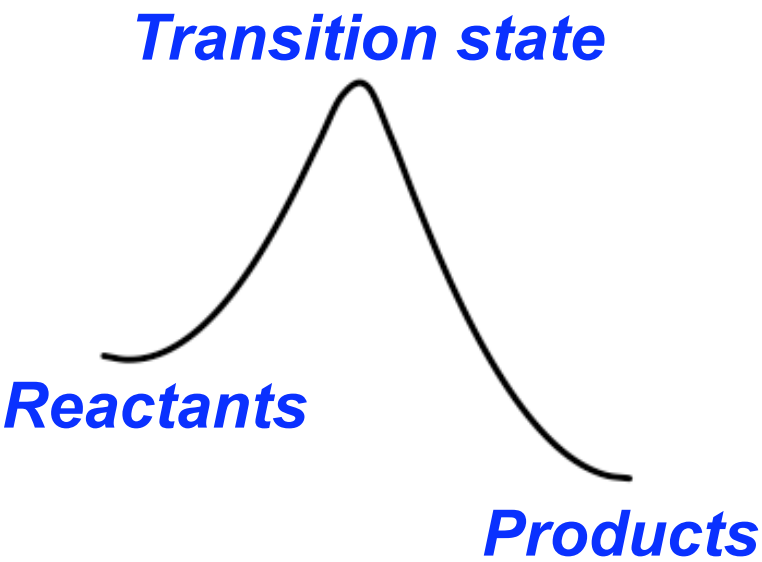
What's Missing?

Validated methods for multistate kinetics

Example

^3O + singlet → singlet

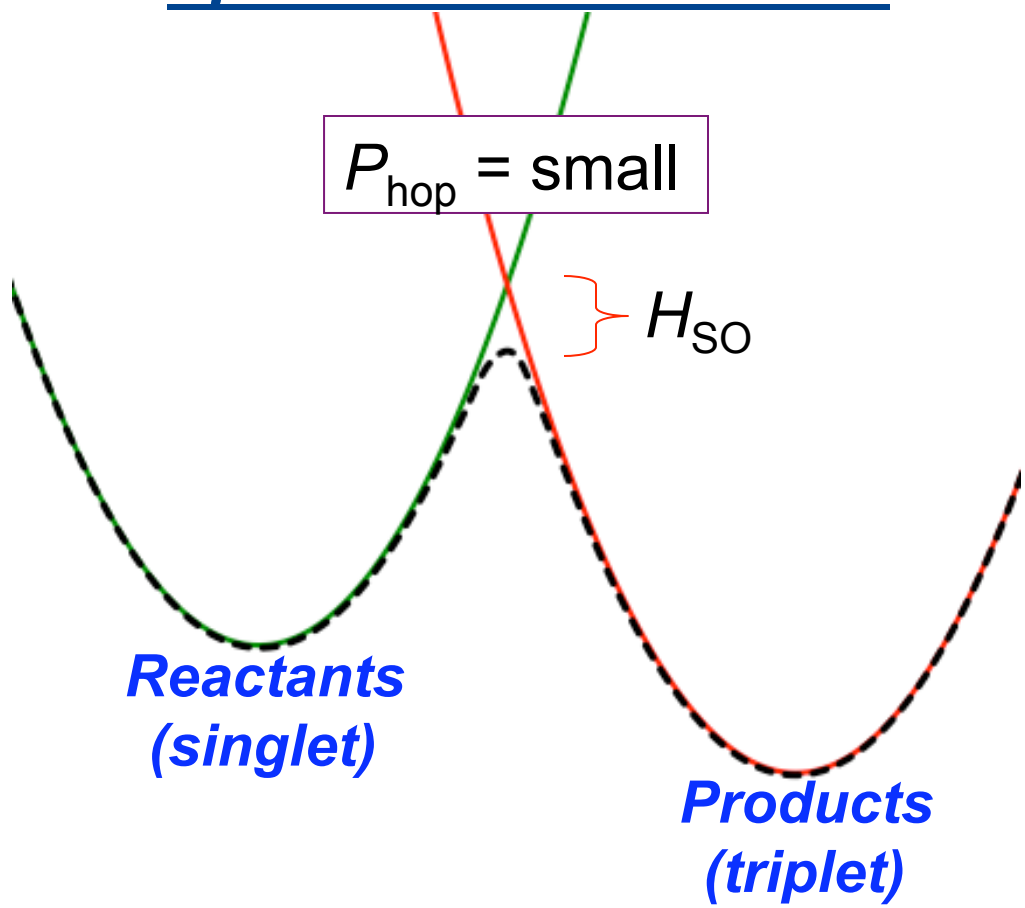
Adiabatic reaction



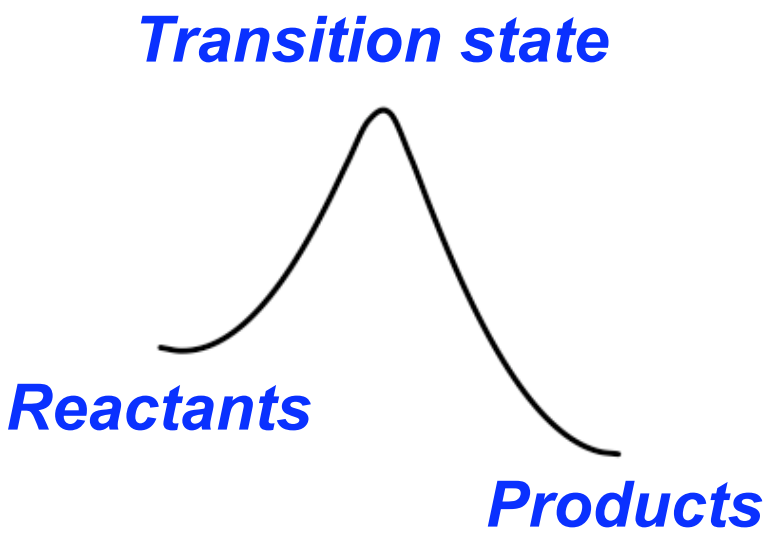
?

≈

Spin-forbidden reaction



Multistate kinetics

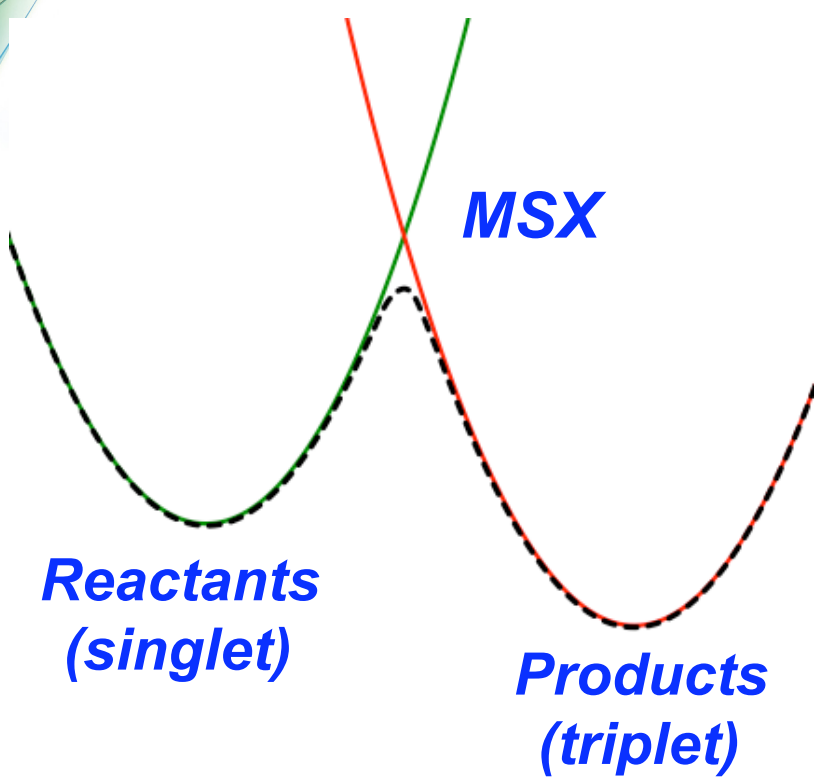


Transition state theory

- $V^{\neq}$ – Saddle point energy
- $N^{\neq}$ – Flux through the TS = state count

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

Multistate kinetics



Jeremy Harvey
Keiji Morokuma
Don Thompson
Miller, Tully, Schatz, Truhlar, etc…

Nonadiabatic "TST"

- V_{MSX} – Minimum on the crossing seam
- N_{MSX} – Flux through the crossing seam

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

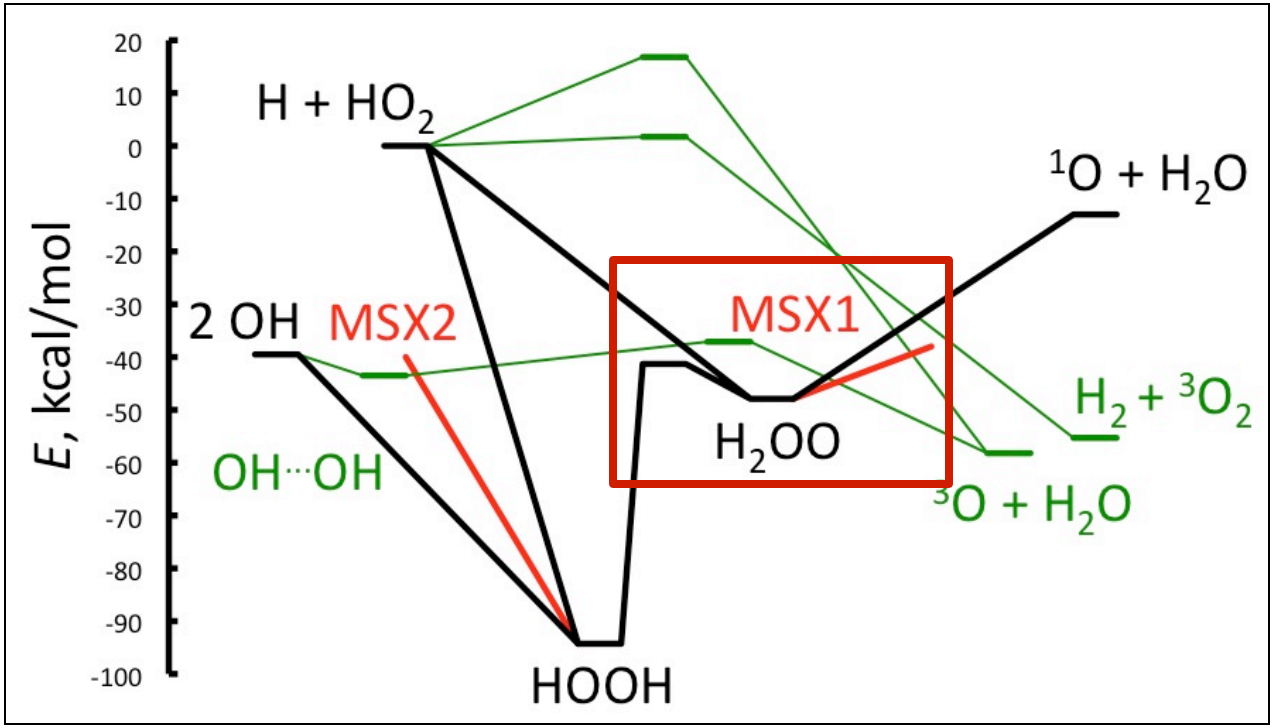
$$N_{MSX}(E) = \int d\varepsilon\, \rho_{SX}(\varepsilon\, P_{hop}(E-\varepsilon)$$

P_{hop} = 1 recovers TST

Spin-forbidden chemistry

Example: H + HO_2

PES – singlet – triplet



Burke et al.

IJCK (2011)

2 OH	95-59%
$H_2 + O_2$	3-39%
$H_2O + {}^1O$	2%
$H_2O + {}^3O$	0%

Small increases in branching to $H_2O + O$ significantly affected modeling

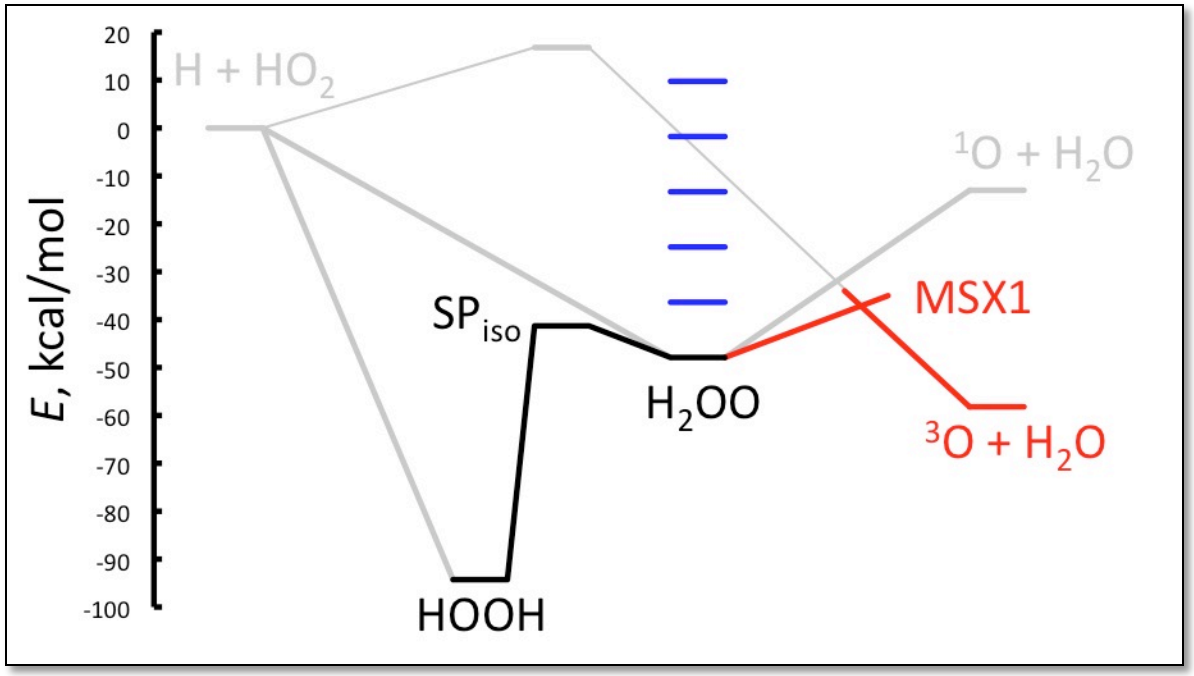
MSX1: $H + HO_2 \rightarrow HOOH^* \rightarrow H_2OO^* \rightarrow {}^3O + H_2O$

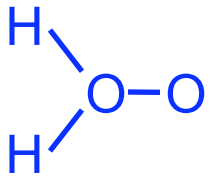
MSX2: $H + HO_2 \rightarrow HOOH^* \rightarrow {}^3OH\cdots OH \rightarrow {}^3O + H_2O$

MSX1: Branching in H_2OO^*

Competition between isomerization (iso)

and spin-forbidden (SF) intersystem crossing

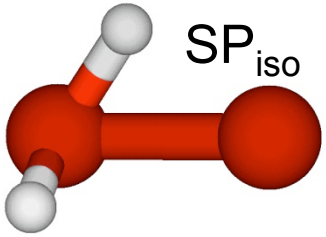


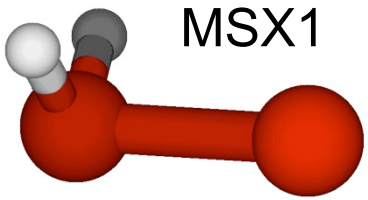


$N_{NA} \rightarrow {}^3O + H_2O$

$N_{iso} \rightarrow HOOH$

$$P_{NA} = \frac{N_{NA}}{N_{NA} + N_{iso}}$$



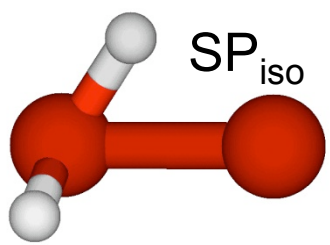


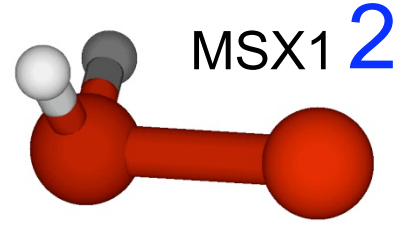
Quantum Chemistry: MSXs vs SPs

Challenges

- The local vicinity of an SP is "flat" ($\nabla V = 0$)
  For an MSX $\nabla V_S \neq 0,\ \nabla V_T \neq 0$
- Singlet-triplet gaps can be challenging to calculate accurately
- Bigger basis sets required for excited states

	$E(SP_{iso})$, kcal/mol				$E(MSX_1)$, kcal/mol				DIFF
Method	ADZ	ATZ	AQZ	CBS	ADZ	ATZ	AQZ	CBS	CBS
MP2	7.5	7.4	7.5	7.6	9.4	12.5	13.2	13.7	6.1
M06-2x	8.8	8.8	8.9	9.0	9.2	9.8	10.0	10.2	1.2
QCISD(T)	6.0	6.2	6.5	6.6	4.8	7.4	8.0	8.4	1.8
CASPT2 (6,6)	5.6	5.6	5.8	5.9	4.6	6.8	7.3	7.6	1.7
CASPT2 (FV)	4.8	4.6	4.7	4.8	6.4	8.5	8.9	9.2	4.4
MRCI+Q (6,6)	6.1	6.4	6.7	6.9	5.2	7.9	8.5	9.0	2.1
MRCI+Q (FV)	5.3	5.1	5.3	5.5	5.5	8.0	8.8	9.3	3.8
				5.9 ± 0.8				8.7 ± 0.7	

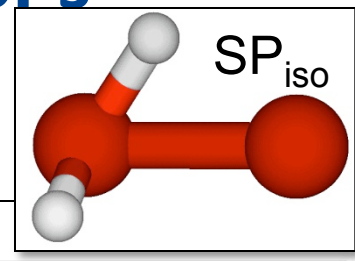


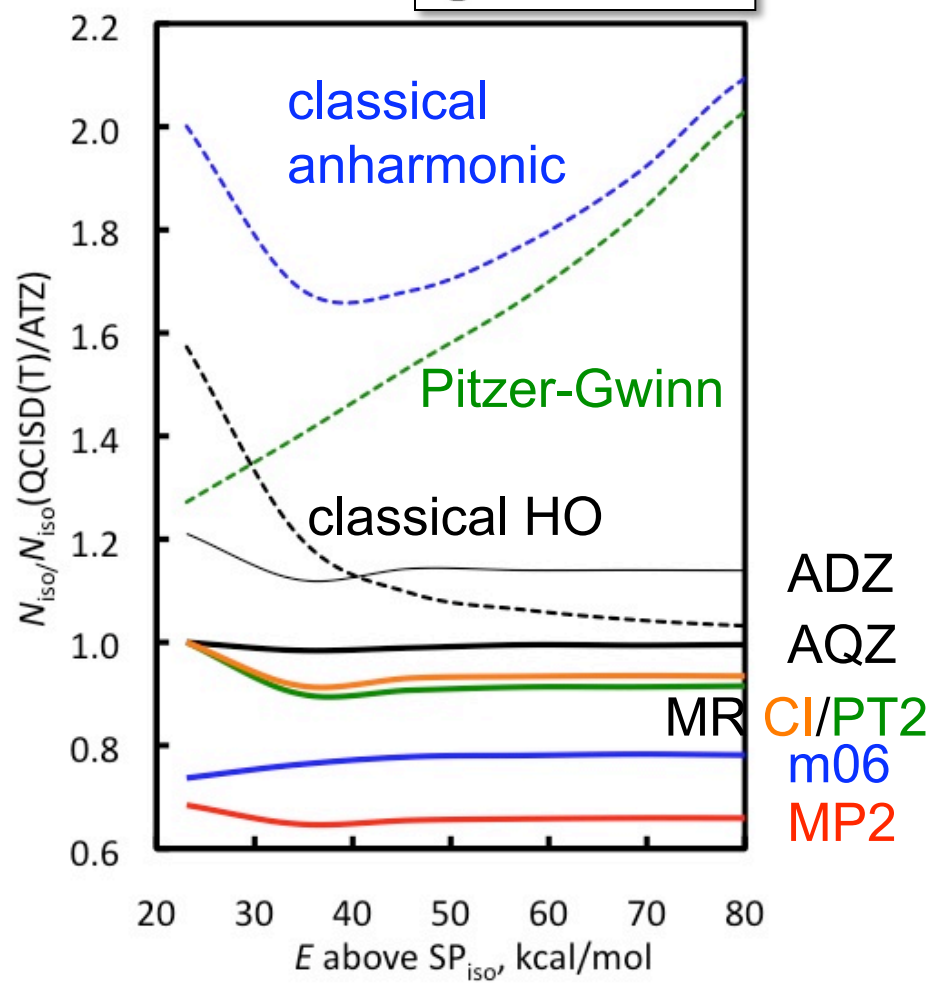


2.7 ± 1.3

Counting States: MSXs vs SPs

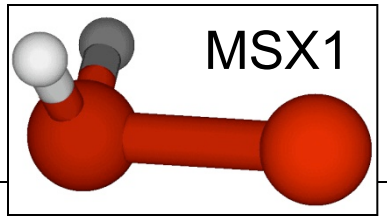
		relative to quantal HO QCISD(T)/ATZ	
quantal HO: basis set			
Beyer-Swinehart direct counts	ADZ	20%	small
	AQZ	< 2%	
method			
	MP2	-30%	
	m06-2x	-20%	small
	MRCI+Q	< -10%	
	CASPT2	< -10%	
classical HO	*Monte Carlo sampling*	60-0%	
classical anharmonic		70-100%	
Pitzer-Gwinn (~quant. an.)		20-100%	big!

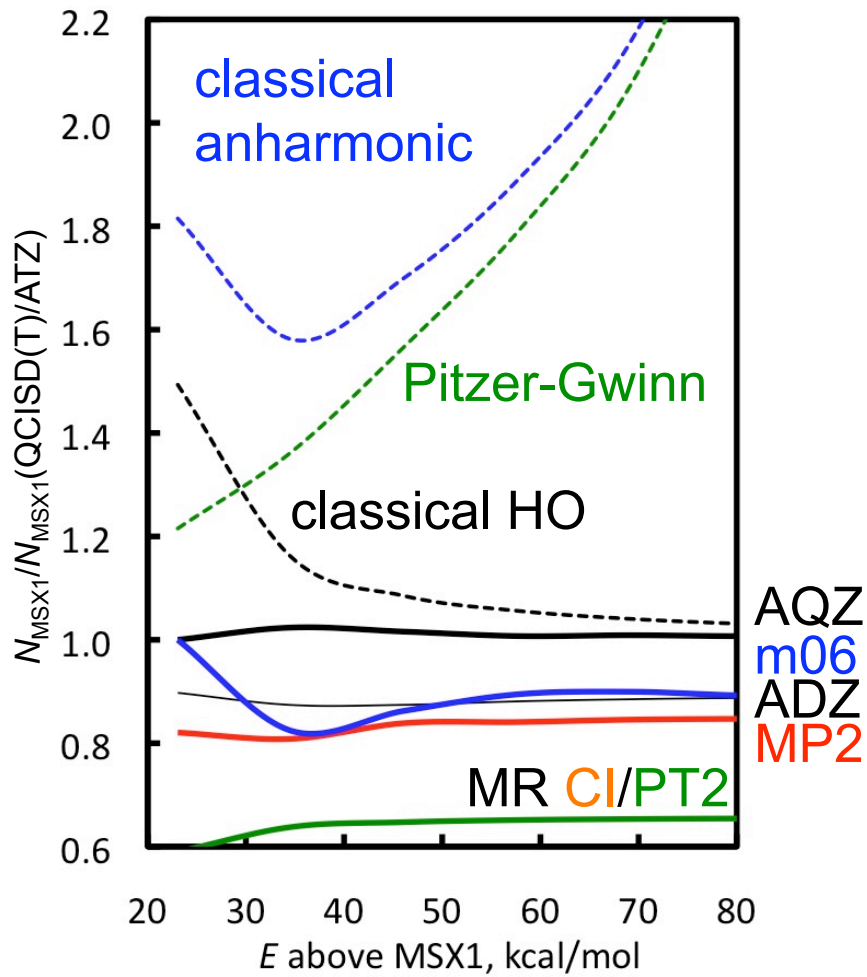




Counting States: MSXs vs SPs

		relative to quantal HO QCISD(T)/ATZ	
quantal HO: basis set			
Beyer-Swinehart direct counts	ADZ	-15%	small
	AQZ	< 2%	
	method		
	MP2	-20%	
	m06-2x	-10%	
	MRCI+Q	-60% !	big!
	CASPT2	-40% !	
classical HO	*Monte Carlo sampling*	50-0%	
classical anharmonic		60-140%	
Pitzer-Gwinn (~quant. an.)		20-140%	big!





MSX frequencies

Because $\nabla V \neq 0$ *,*

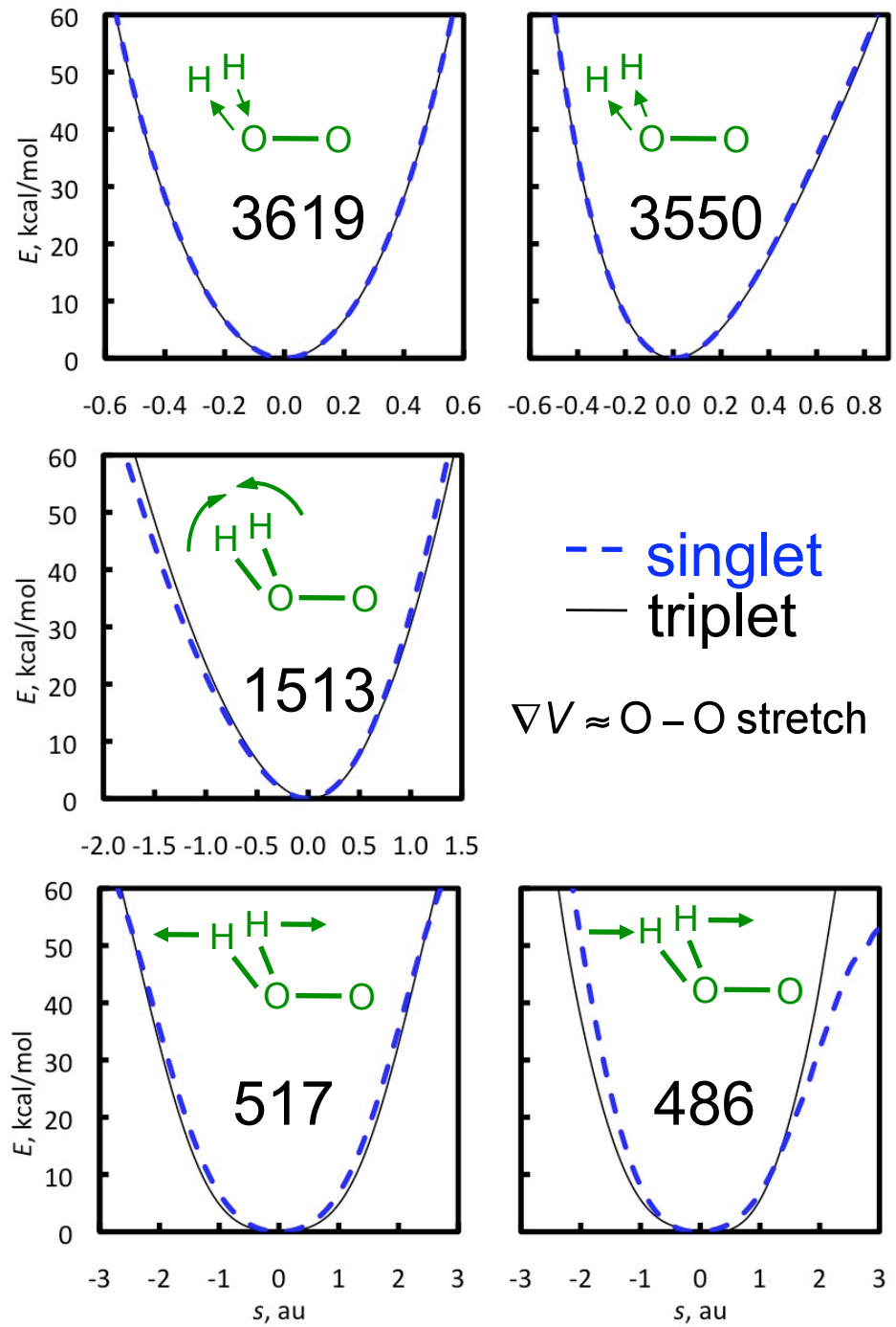
- *frequencies are not invariant to coordinate system*
- *singlet and triplet frequencies do not agree*

QCISD(T)/ATZ
MSX1 frequencies (cm^{-1})

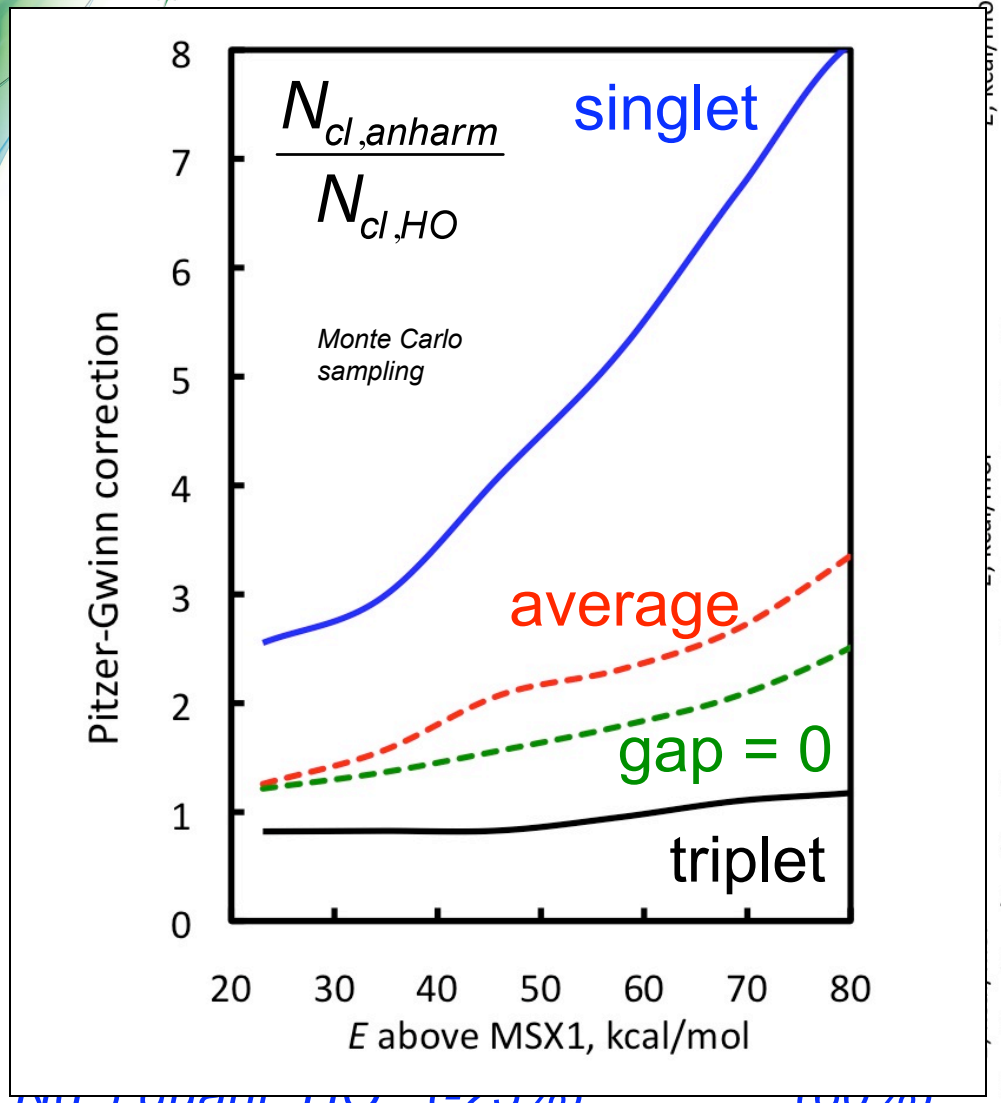
Average	Singlet	(% diff)	Triplet	(% diff)
486	538	(11)	430	(-11)
517	571	(10)	455	(-12)
1513	1508	(-0.3)	1518	(0.3)
3550	3560	(0.3)	3541	(-0.3)
3619	3625	(0.2)	3612	(-0.2)

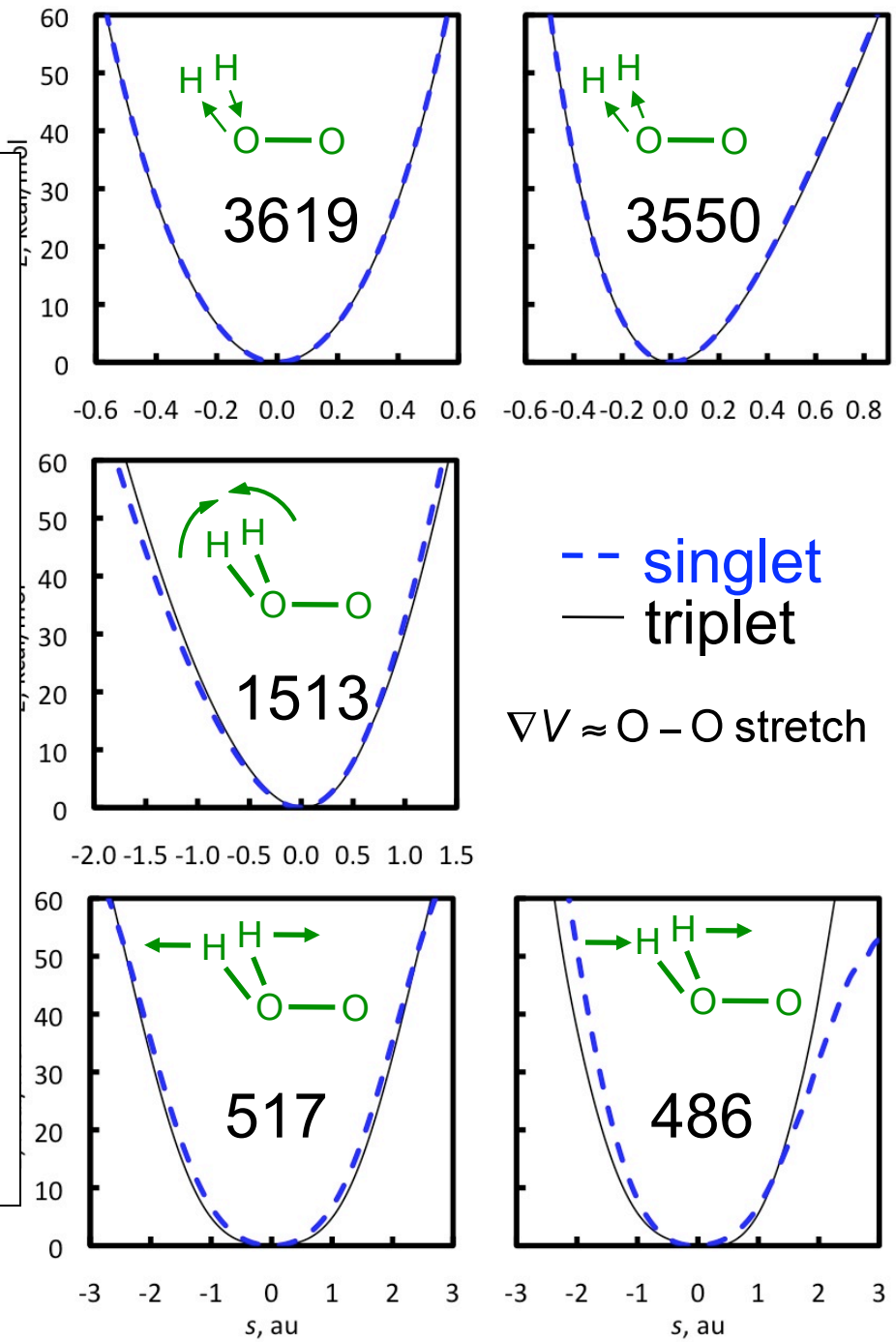
N(E) quant. HO: (-25%) (60%)

Beyer-Swinehart direct counts



MSX frequencies





Beyer-Swinehart direct counts

Hopping probability

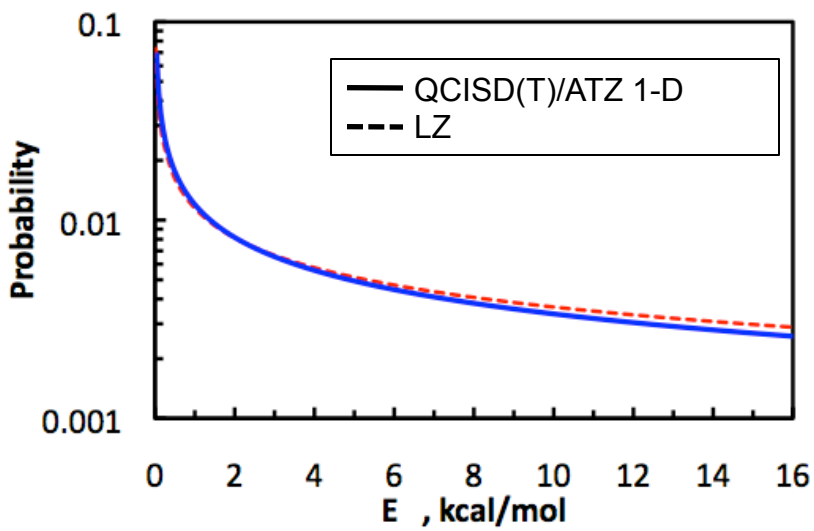
Landau-Zener

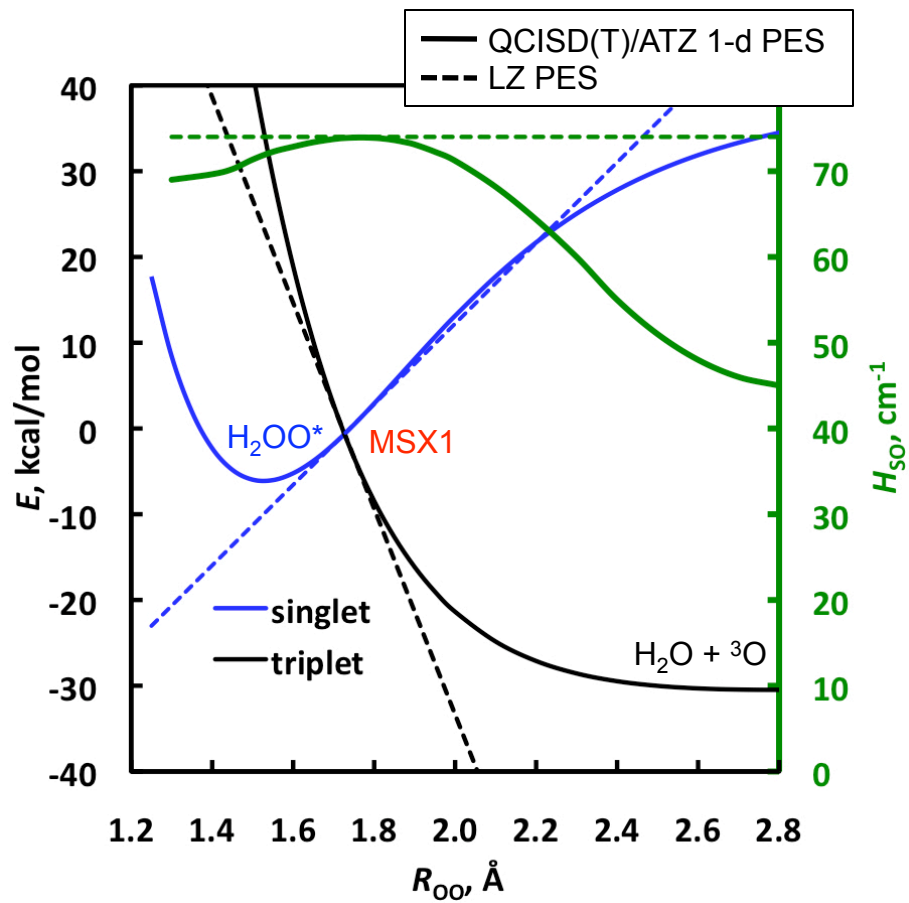
$$P_{LZ} = 1 - \exp\left(\frac{-2\pi H_{SO}^2}{\hbar |\nabla V| v_\perp}\right)$$

H_{SO}	spin-orbit coupling (~75 cm^{-1})
$\lvert\nabla V\rvert$	norm of gradient of the gap
$v_\perp$	velocity perpendicular to seam (=$\sqrt{2E/\mu}$ in 1-d)

- 1-dimensional NA dynamics
- Constant H_{SO} and $|\nabla V|$

LZ formula is OK in 1-D





Non-Born-Oppenheimer MD

Non-BO MD: Equations of motion

- Nuclear d.o.f. (classical)

$$\dot{p} = -\nabla V_{eff}(x, c_i)$$
$$\dot{x} = p / m$$

- Electronic d.o.f. (quantal)

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

Solve the Schrödinger equation along a time-dependent trajectory $[x(t), p(t)]$

$$i\hbar \dot{c}_i = \sum_j c_j \left(U_{ij}(x) - i\hbar p \cdot d_{ij}(x) / m \right)$$

U_{ij} and d_{ij} are potentials & couplings dependent on x

nuclear d.o.f. affect electronic d.o.f.

need electronic → nuclear feedback

Two strategies for e → n feedback

Mean field: $V_{eff} = \sum_i \rho_{ii} V_i$

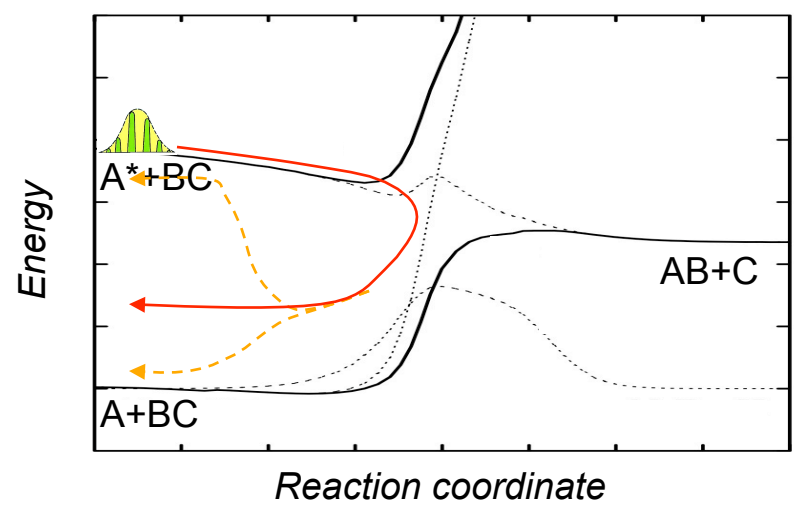
Original: Semiclassical Ehrenfest (SE)

Improved: Coherent switches with decay of mixing (CSDM)

$\rho_{ij} \to 1$ or 0 as $t \to \infty$ (decoherence)

Stochastically, dynamically choose final state

Characteristic decoherence rate



Testing the "2 pass" assumption

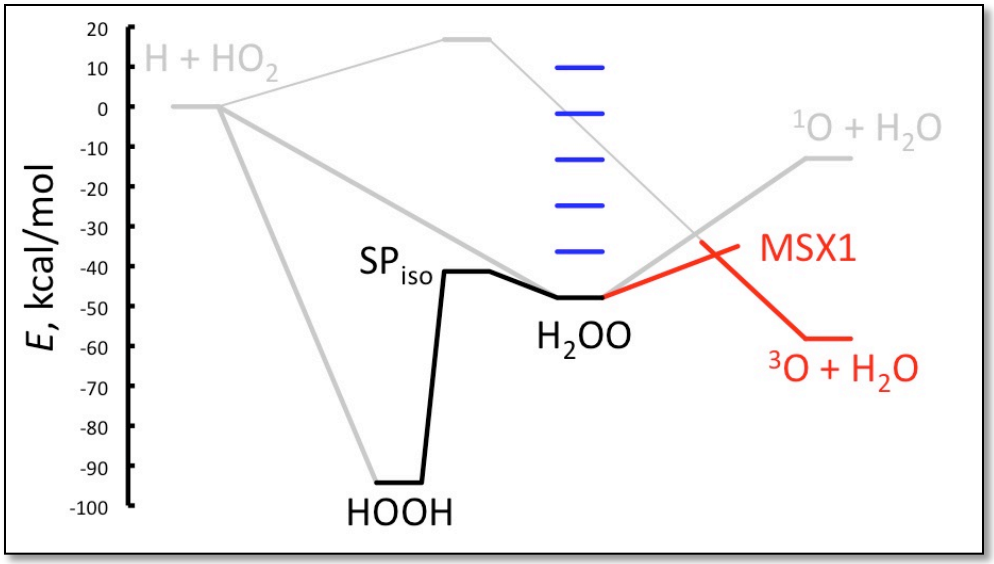
H_2OO^* → products

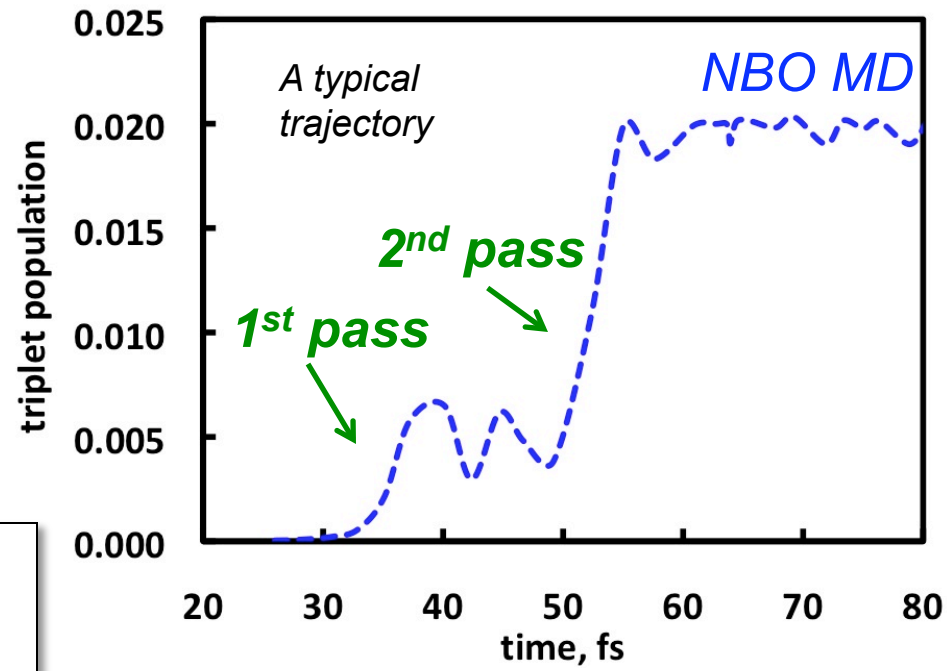
Direct MP2/cc-pVDZ trajectories

E_{tot} = 15 – 45 kcal/mol relative to H_2OO^*

Watch for HOOH or H_2O + O formation

Monitor seam crossings





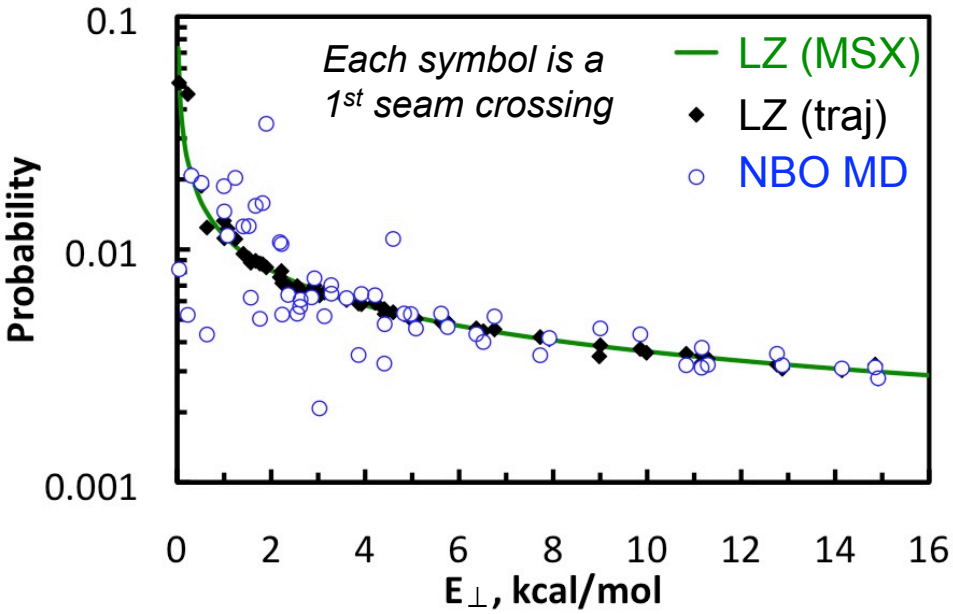
Passes	% of trajectories
0	72
1	3
2	22
3	0
4	3

These start near the seam

OK

Test of the 1-d approximation

1st passes from 250 NBO MD trajectories



LZ (traj) – Evaluated with instantaneous trajectory values of H_{SO} and $|\nabla V|$ sampled with trajectories

LZ (MSX) – Evaluated with MSX values

<10% error ***OK***

NBO MD – Full dimensional dynamics

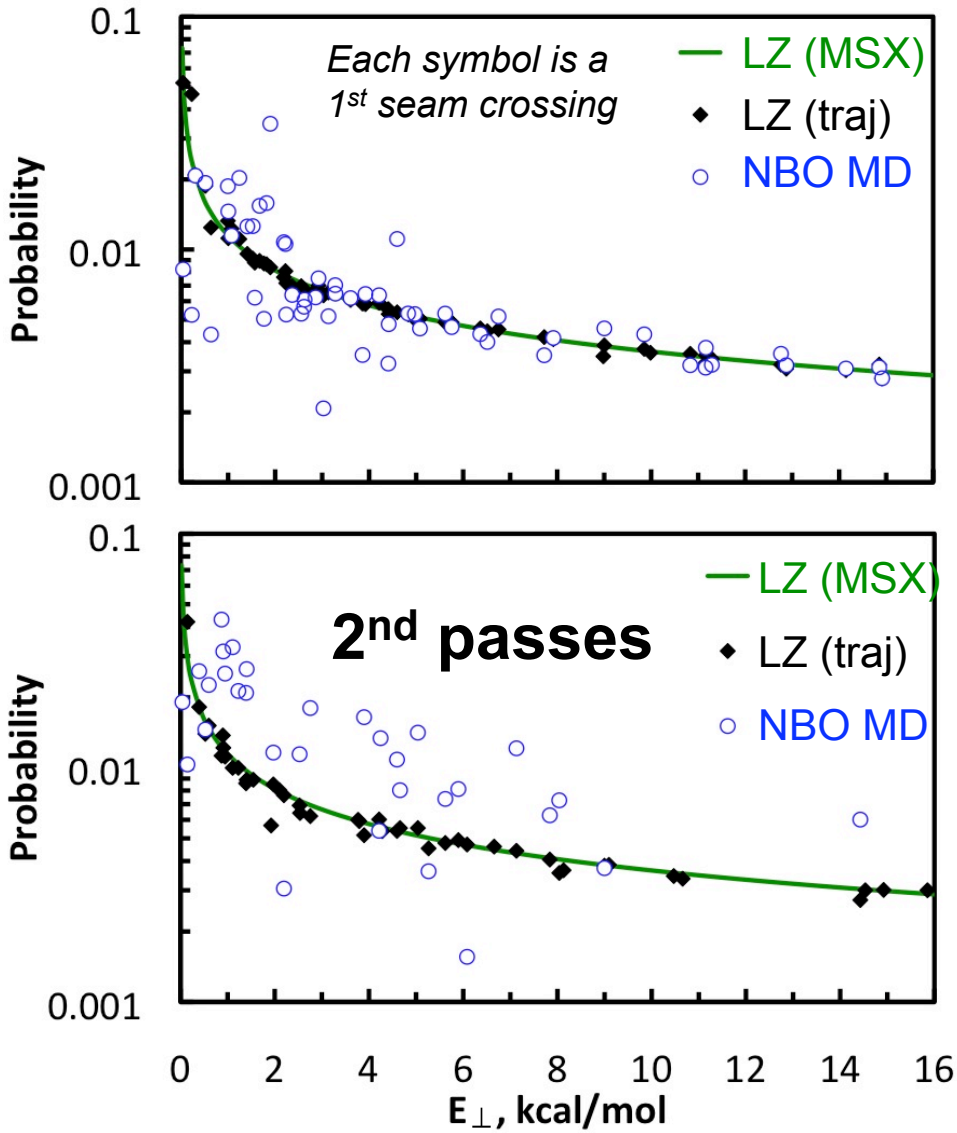
~30% difference
larger at low E
3x maximum difference

not OK

Error in the 1-d approach is due to energy exchange with E_{LZ} during the NA event, not due to the geometry dependence of the properties of the seam.

Test of the 1-d approximation

1st passes from 250 NBO MD trajectories

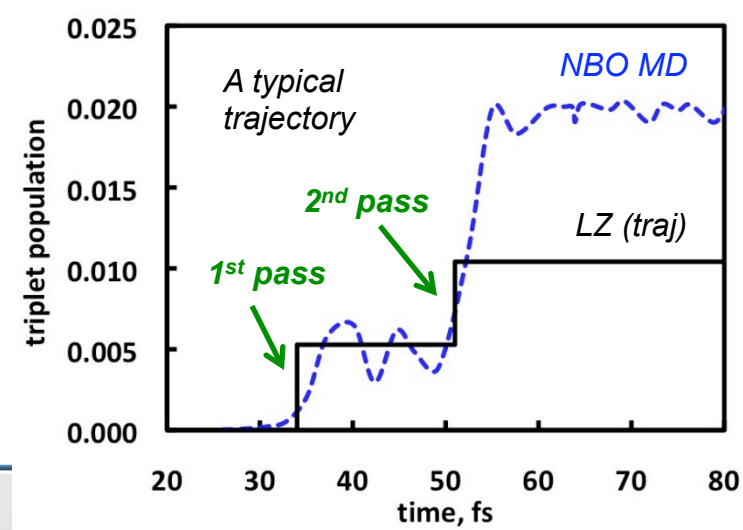


LZ (traj) – Evaluated with instantaneous trajectory values of H_{SO} and $|\nabla V|$ sampled with trajectories

LZ (MSX) – Evaluated with MSX values
<10% error

NBO MD – Full dimensional dynamics
~30% difference
larger at low E
3x maximum difference

Error in 2nd pass is 3x larger due to coherence



H_2OO^* product branching & error accounting

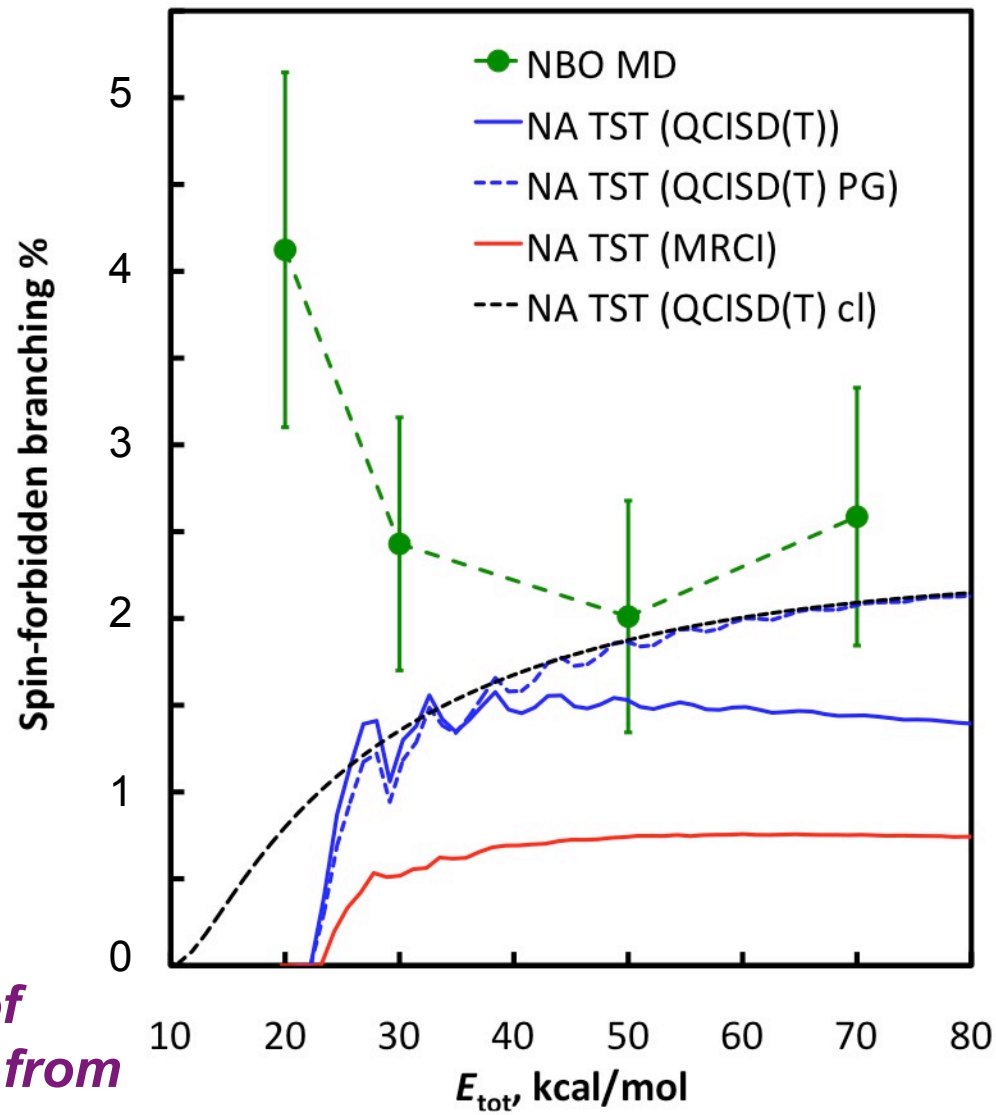
NBO MD

NA TST

- *Quantal HO*
- *QCISD(T)/ATZ*
- *2 pass Landau-Zener*

Uncertainties

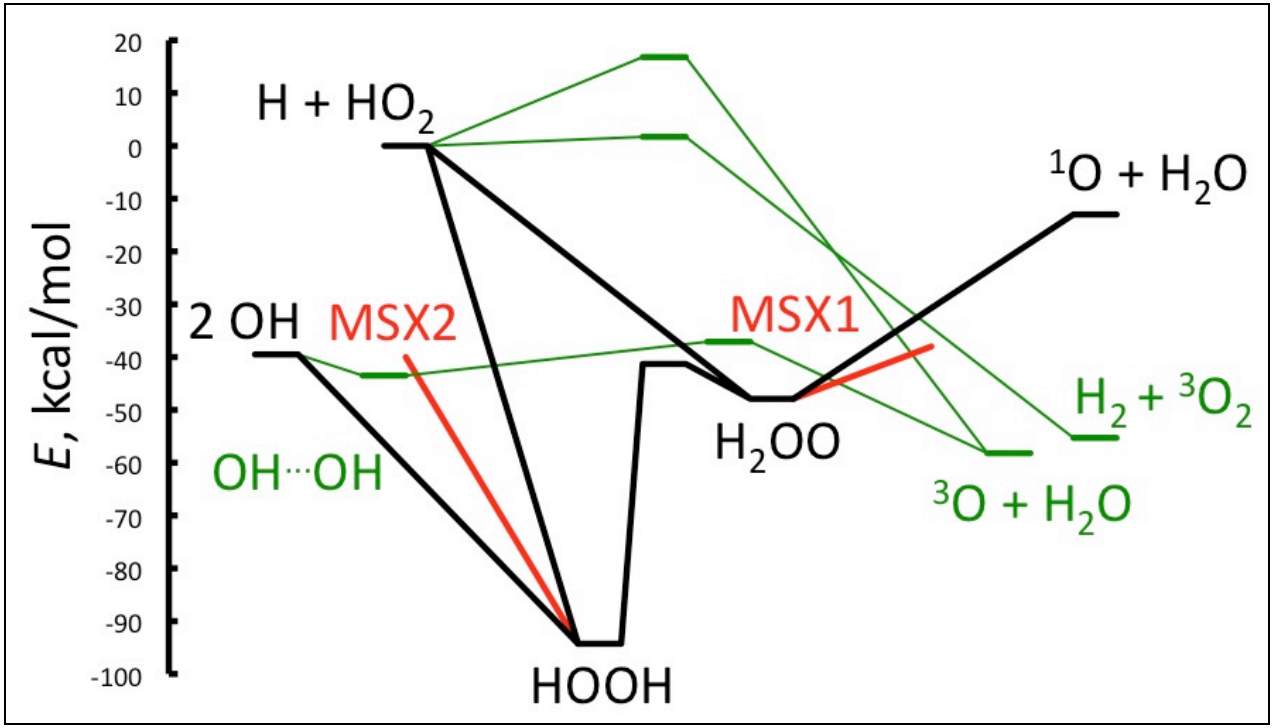
- *Quantum chemistry: up to 2x*
- *Vibrational anharmonicity: 0-40%*
- *1-D LZ: up to 2x at low E_{tot}*



NA TST has all the uncertainties of TST, with additional uncertainties from quantum chemistry and the LZ approx.

Results: Spin-forbidden pathways

PES – singlet – triplet – forbidden



Spin-allowed theory	
2 OH	93-58%
$H_2 + O_2$	4-37%
$H_2O + {}^1O$	2%
$H_2O + {}^3O$	0%

MSX1: $H + HO_2 \rightarrow (\ HOOH^* \rightarrow)\ H_2OO^* \rightarrow {}^3O + H_2O$ 1% !

MSX2: $H + HO_2 \rightarrow HOOH^* \rightarrow {}^3OH\cdots OH \rightarrow {}^3O + H_2O$ 1% !

For "first row" molecules, spin-forbidden channels unlikely to compete with spin-allowed channels

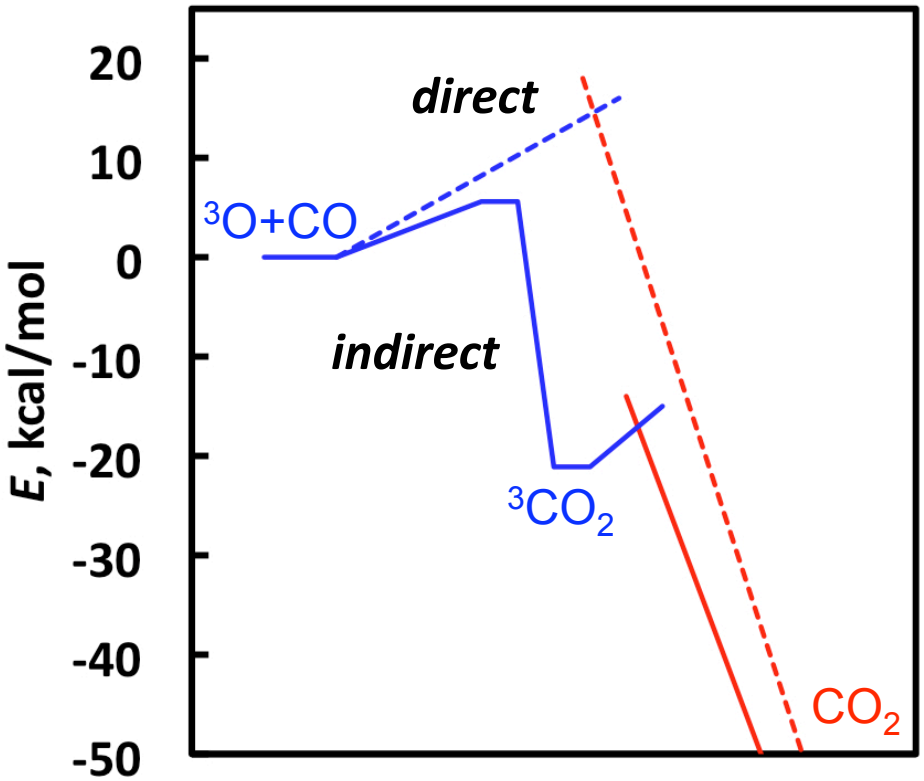
Spin-forbidden kinetics:
Example 2: $^3O + CO$

Oxidation of CO to CO_2

- Previous theory (Mebel et al. 2000)

$^3O + CO$ ➔ collinear MSX ➔ CO_2 ***direct***

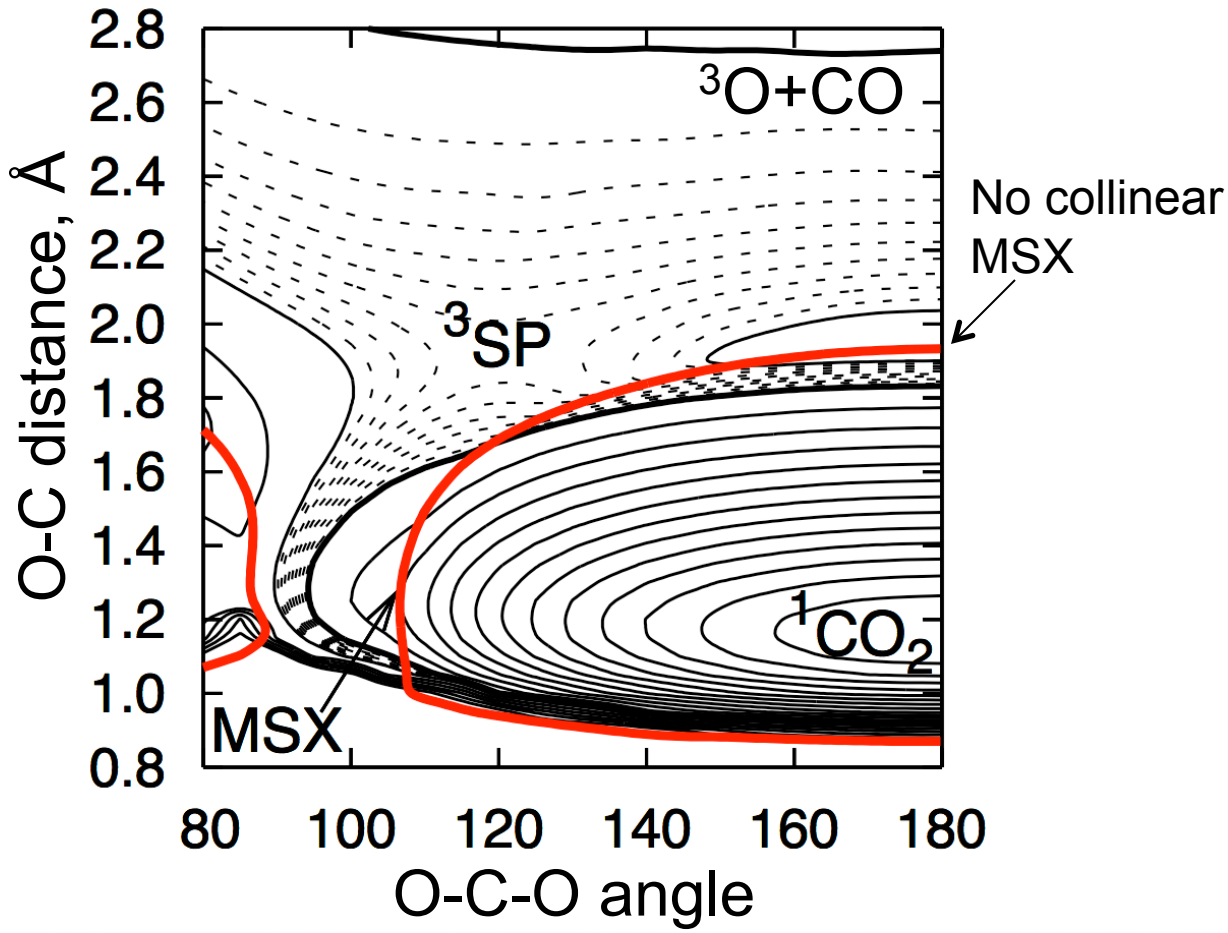
➔ $^3CO_2$ ➔ bent MSX ➔ CO_2 ***indirect***



$^3O + CO$

Dawes
3D analytic IMLS PES
singlet, triplet, coupling
dw-MRCI+Q/CBS

Plot of min(singlet, triplet)



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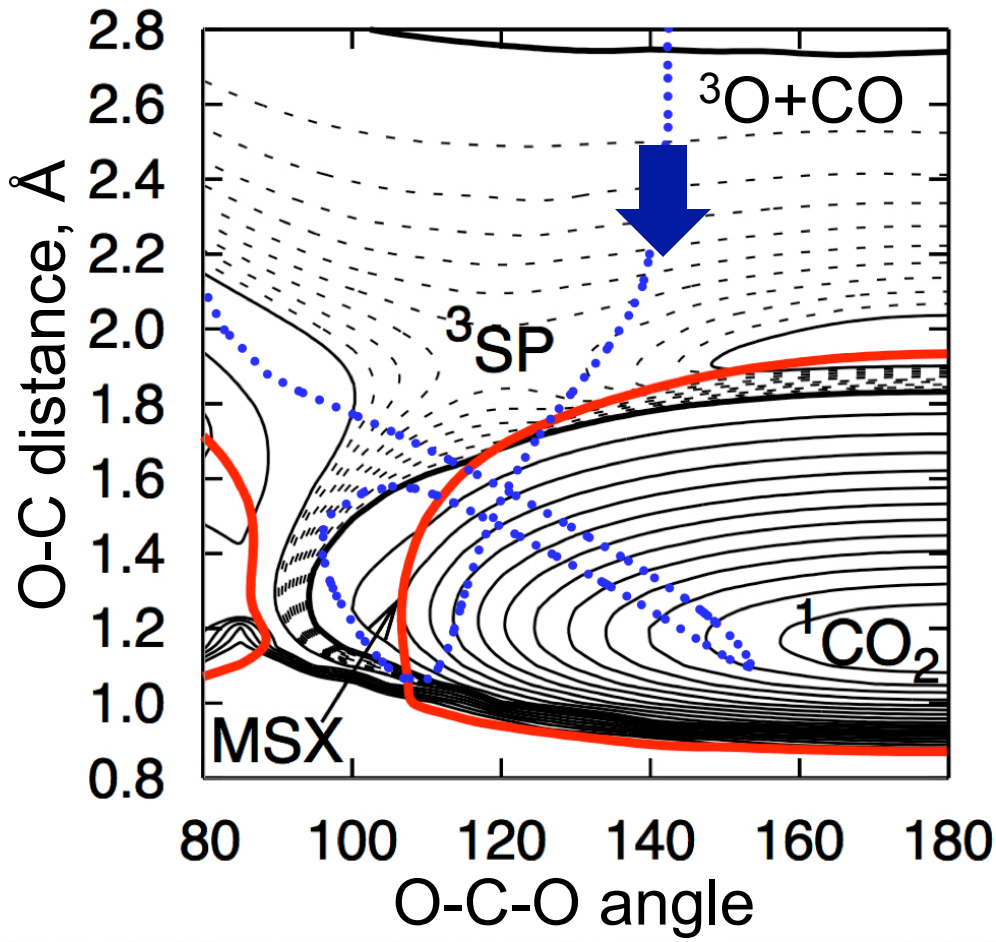
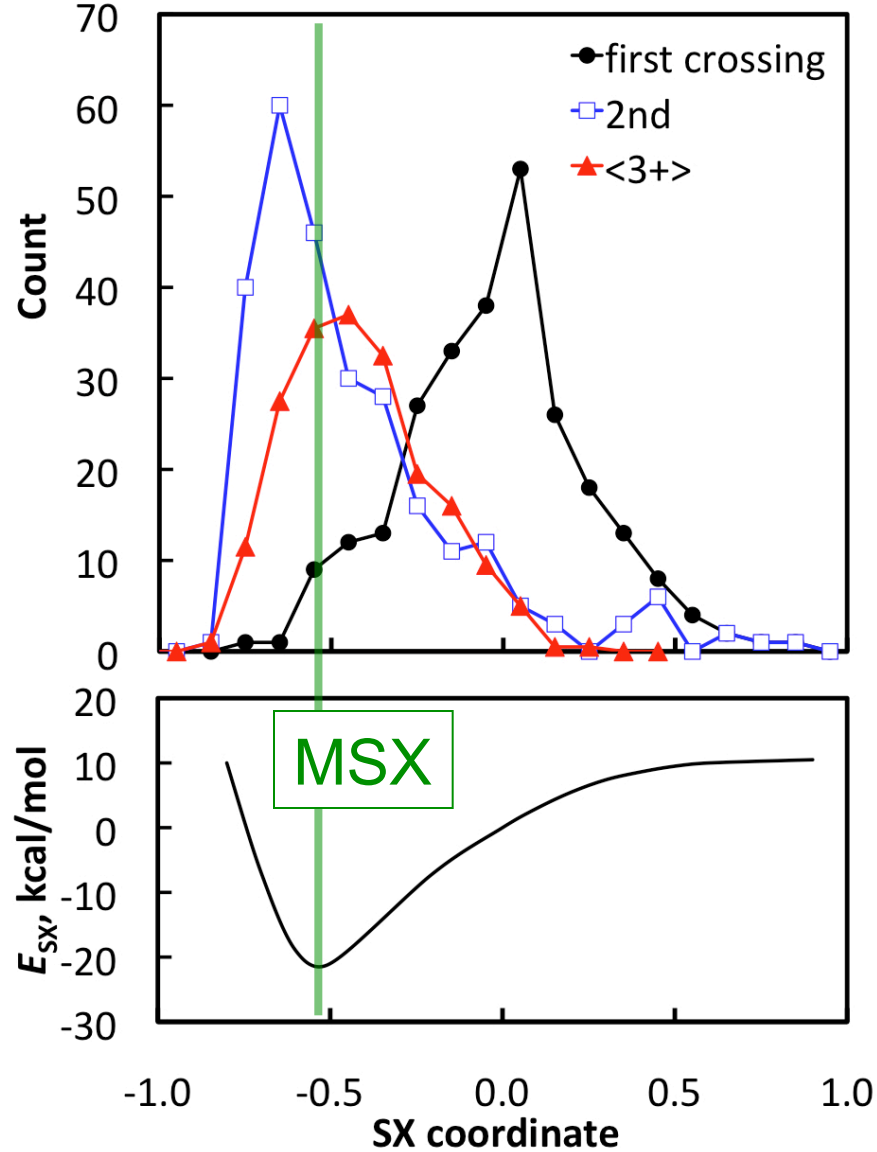


NBO MD



Conclusions

Quantitative theoretical kinetics is possible

- QC: Single reference/multireference quantum chemistry
- TST: Conventional TST, with anharmonicity corrections
- ME: Phenomenological rates from the master equation
- Accuracy: Rates predicted within a factor of ~2 or so, with careful propagations of uncertainties

Development

- **Collisional energy transfer**

  Demonstrated the accuracy of trajectory based predictions of $\alpha = \langle \Delta E \rangle$

  Universal TB+exp/6 can be used to efficiently study large systems, trends
- **Spin-forbidden kinetics**

  NBO MD is a useful tool for studying spin-forbidden processes

  We quantified additional sources of uncertainty in the NA "TST" approach
  - QC: Crossings are more difficult to characterize than saddle points
  - Additional errors due to the 1-D LZ approximation in P_{hop}

END