# Spin-Forbidden Kinetics

Theoretical Kinetics and Non-Born-Oppenheimer Chemistry

Ahren Jasper

# Spin-forbidden chemistry

***Examples***

| | |
|---|---|
| $^3O$ + singlet → singlet | radical + radical → singlet & triplet species |
| $^3O + CO \rightarrow CO_2$ | $H + HO_2 \rightarrow$ products |
| $^3O$ + alkene | $H + NCO \rightarrow$ products |

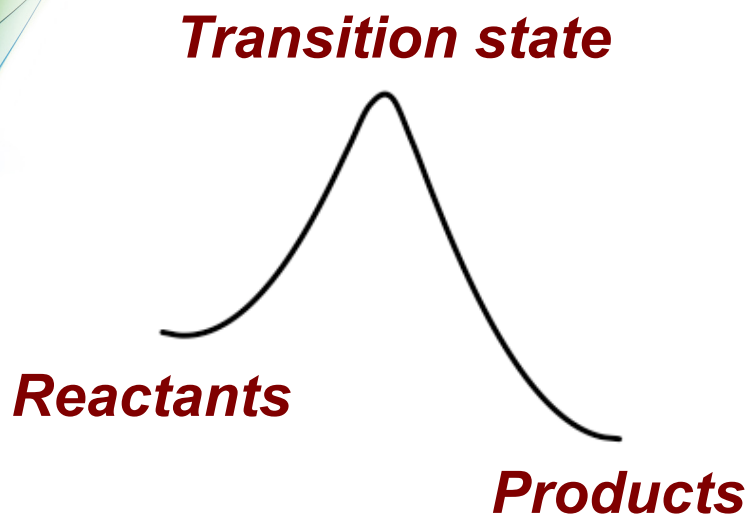
***How accurately can we calculate spin-forbidden rates?***

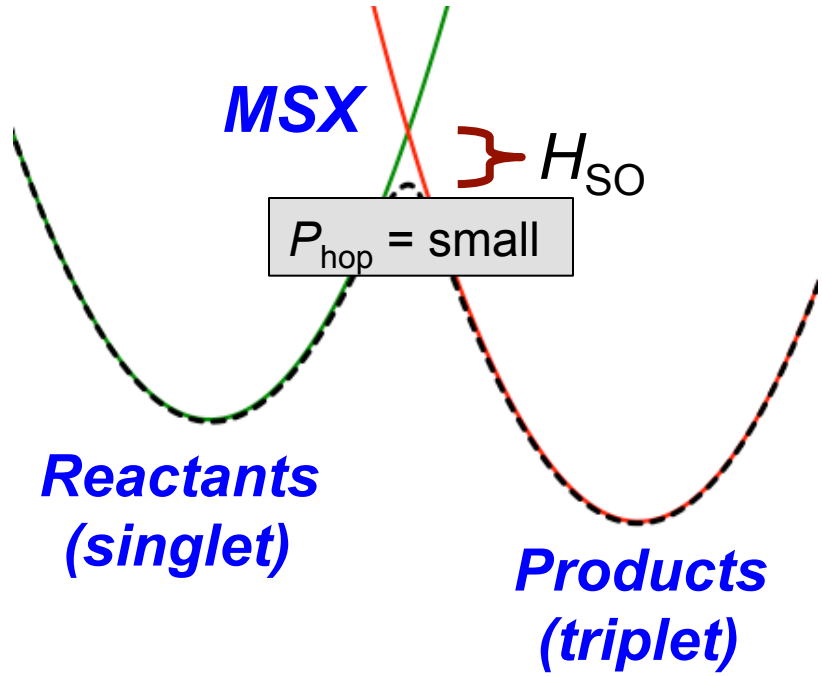
Are the errors due to the **PES** similar to those for spin-allowed kinetics?

What are the errors due to the spin-forbidden theoretical **models**?

# 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

$P_{\mathrm{reac}}$ = 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 |

$E_X$ energy along $\nabla V$

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

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

# Nonadiabatic "transition state theory"

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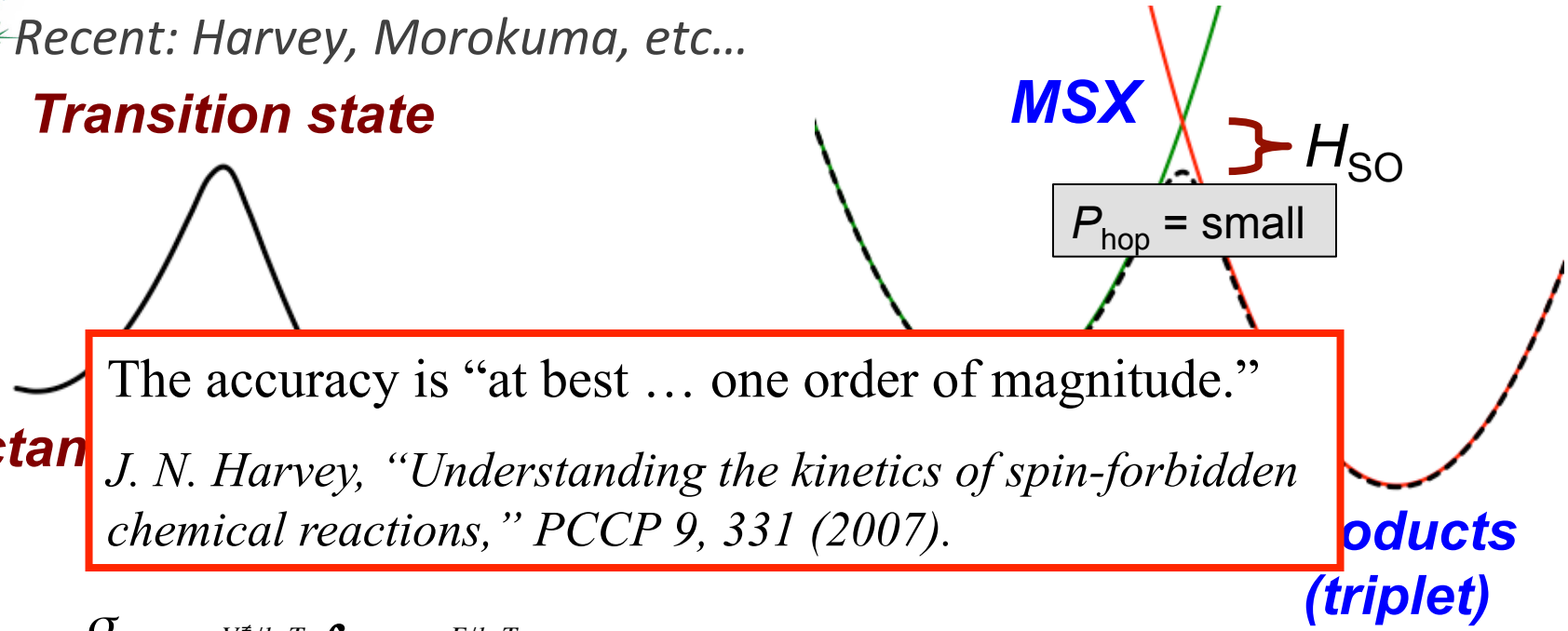


The accuracy is "at best … one order of magnitude."

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

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# Applying NA "TST": H + NCO

**Klippenstein & Harding, PCI 32, 149 (2009)**

Complete theoretical study <u>except</u> for the spin-forbidden kinetics

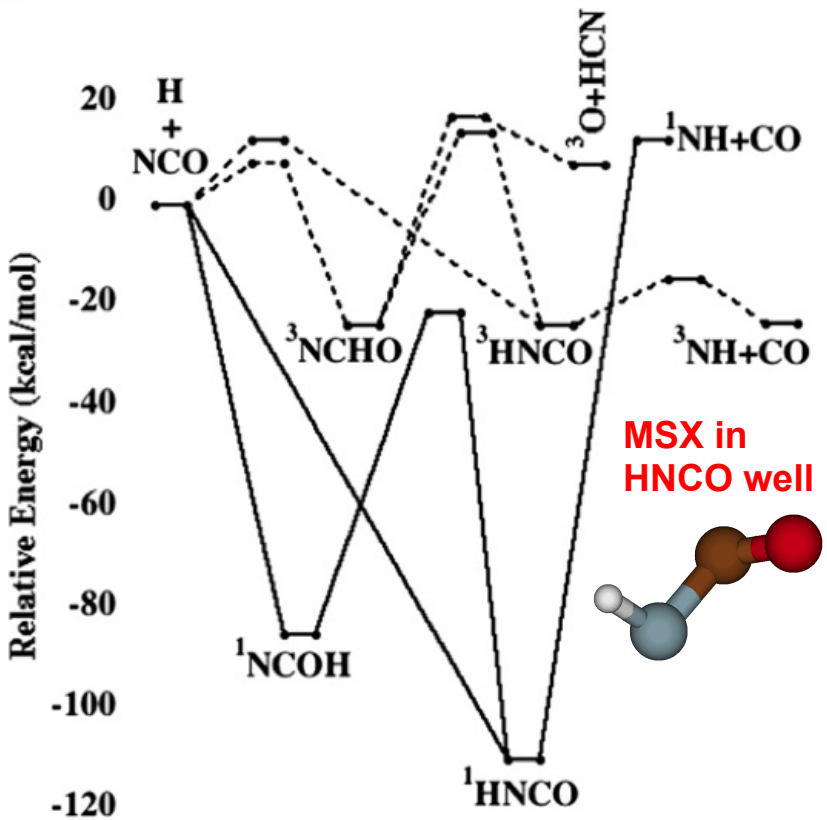
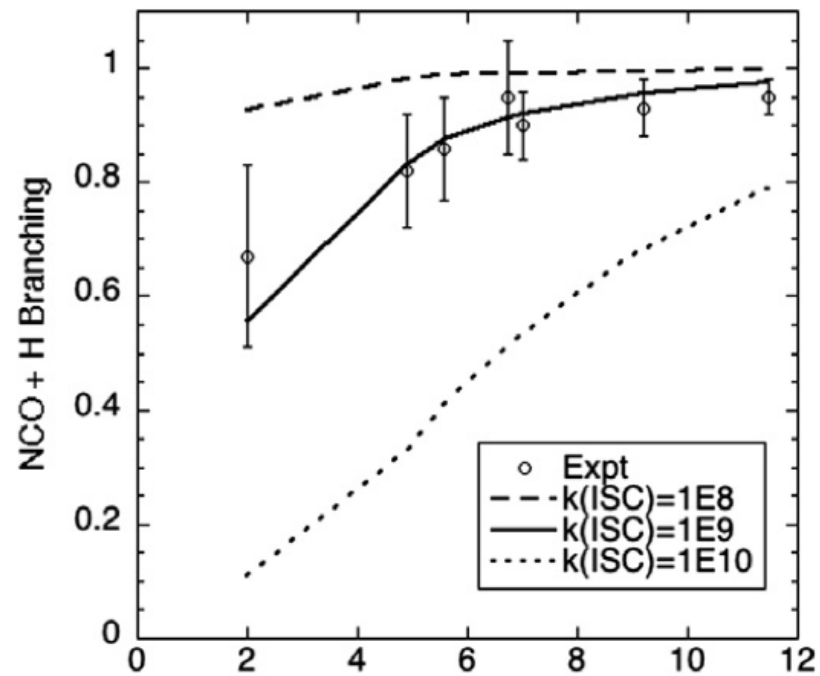



Fig. 1. Schematic diagram of the energies of the stationary points on the HNCO potential energy surface. Solid lines denote singlet states, while dashed lines denote triplet states.

HNCO + $h\nu$ → NCO + H




exp: Berghout, Hsieh, Crim, JCP 114, 10835 (2001)

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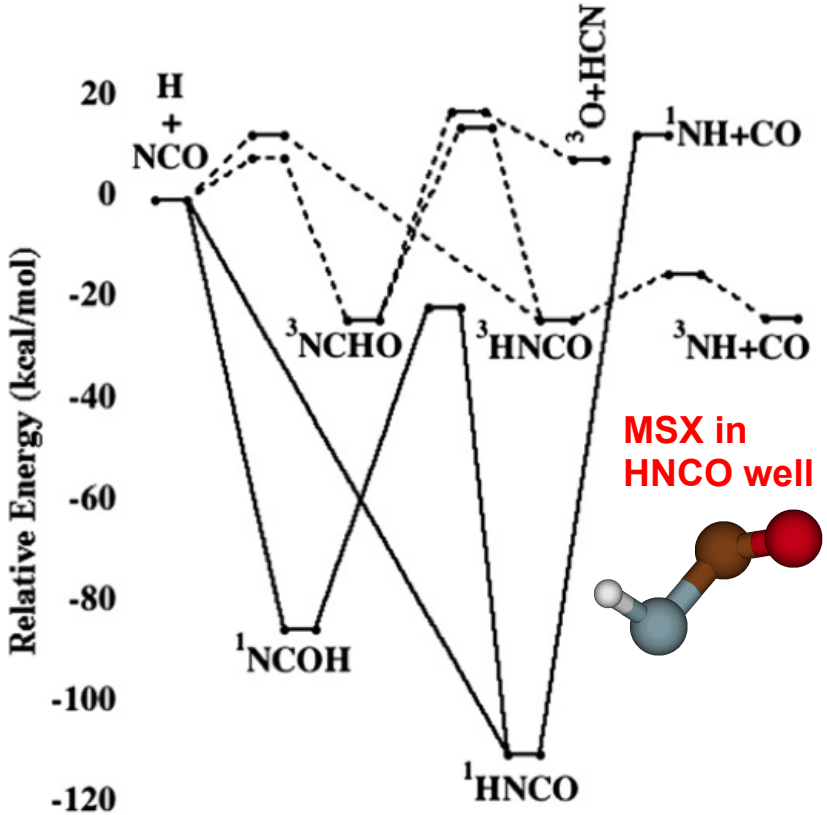


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H + NCO → products

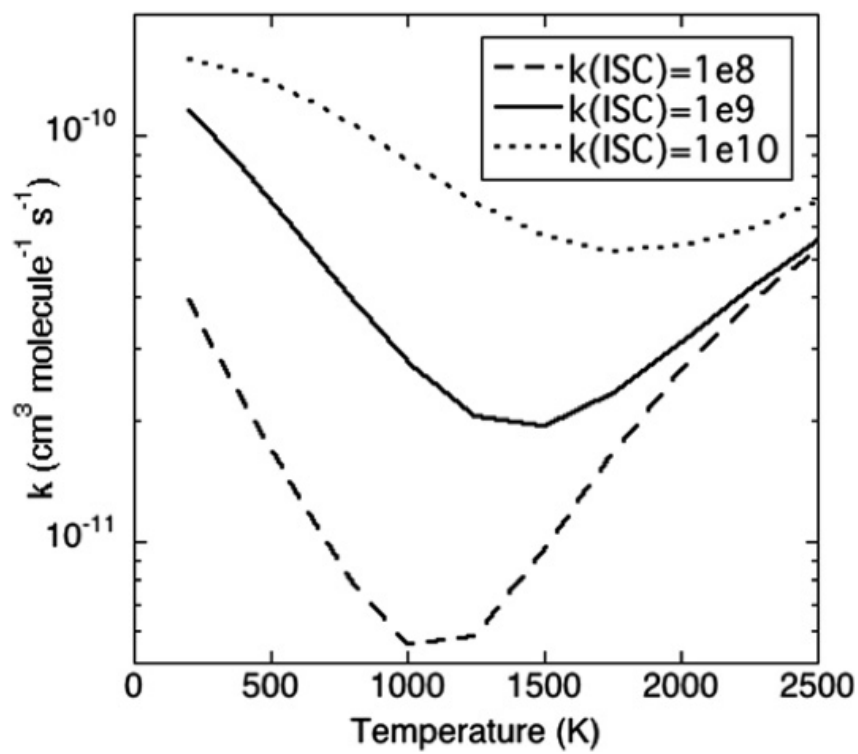


Fig. 7. Plot of the sensitivity of the collisionless limit rate coefficient to the intersystem crossing rate.

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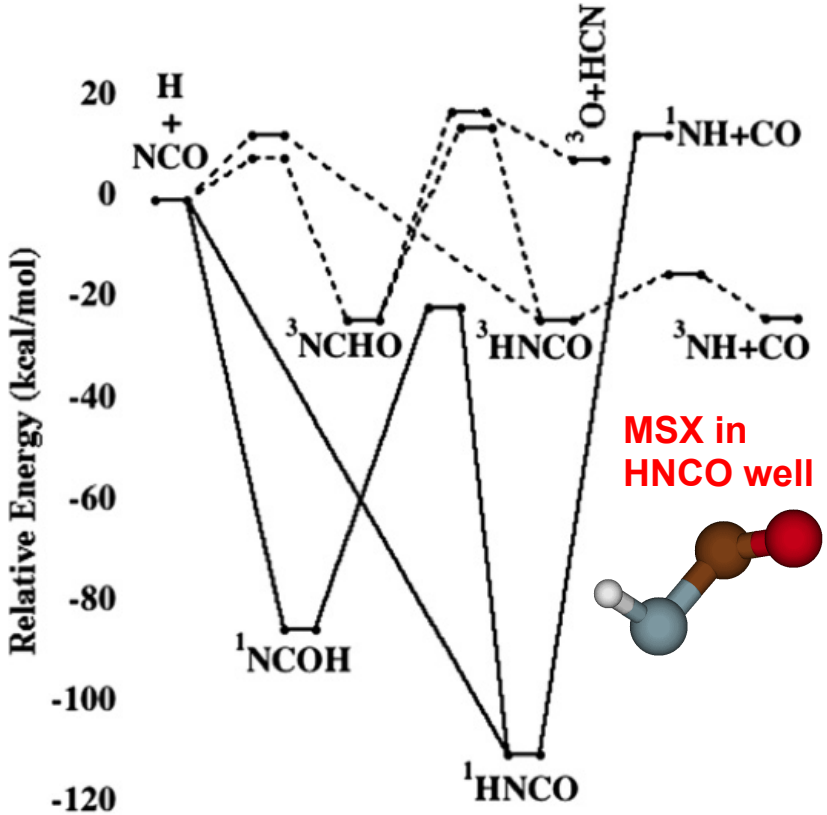


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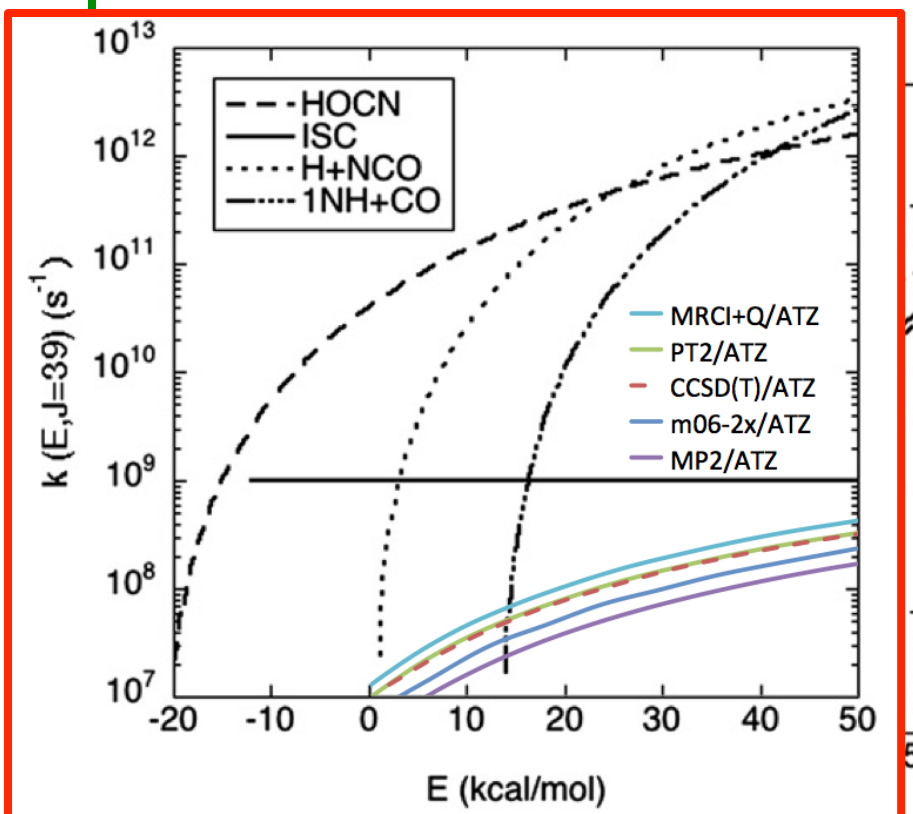



Fig. 4. Plot of the microcanonical rate constants for reaction of HNCO as a function of energy above the H + NCO threshold. The labels denote the product(s) of the reaction.

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

*1974-5 W. H. Miller, J. C. Tully*

***Improved accuracy for spin-forbidden kinetics***

***1. The crossing seam is not a transition state***

*"Two transition state" model breaks down*

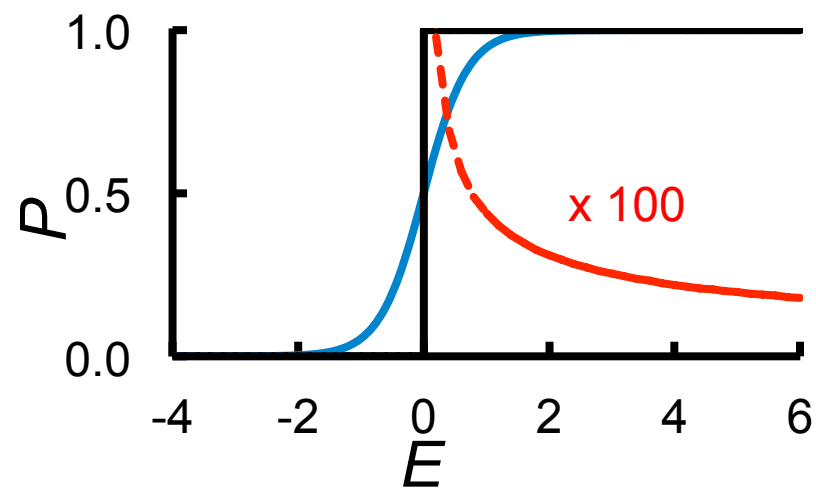
*Nonlocal (history-dependent) electronic dynamics*

*Electronic (de)coherence*

***2. Multidimensional effects in $P_{hop}$***

*Global seam properties*

*Mutidimensional dynamics*




***Examples***

*$H + HO_2$, $O + CO$*

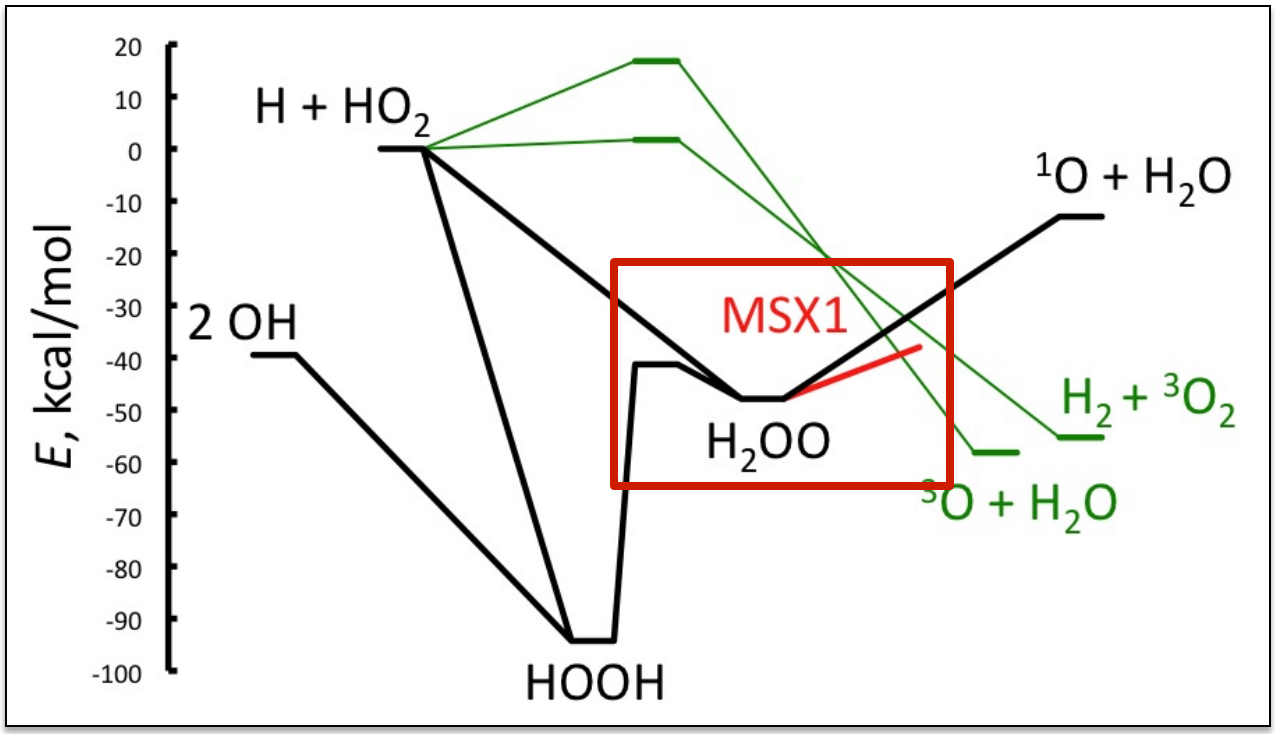
$P_{TST}$ Heaviside (fundamental assumption)

$P_{tunn}$ SCTST, SCT/LCT (multidimensional)

$P_{hop}$ new (multidimensional & nonlocal)

# Error analysis for H + $HO_2$

***PES – singlet – triplet***

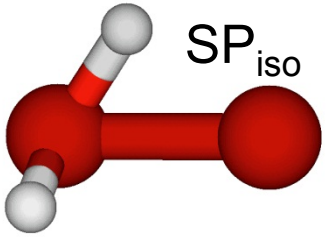


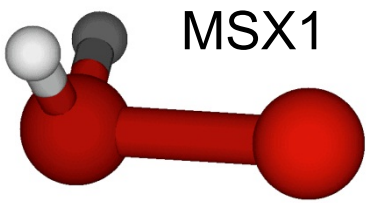

Burke, Chaos, Ju, Dryer, Klippenstein, IJCK (2011)

| | |
|---|---|
| 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**

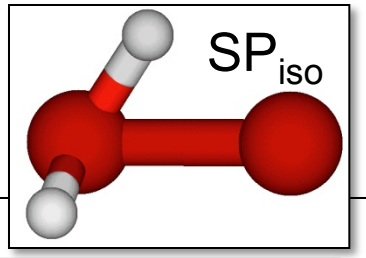
MSX1: $H + HO_2 \rightarrow HOOH^* \rightarrow H_2OO^* \rightarrow {}^3O + H_2O$



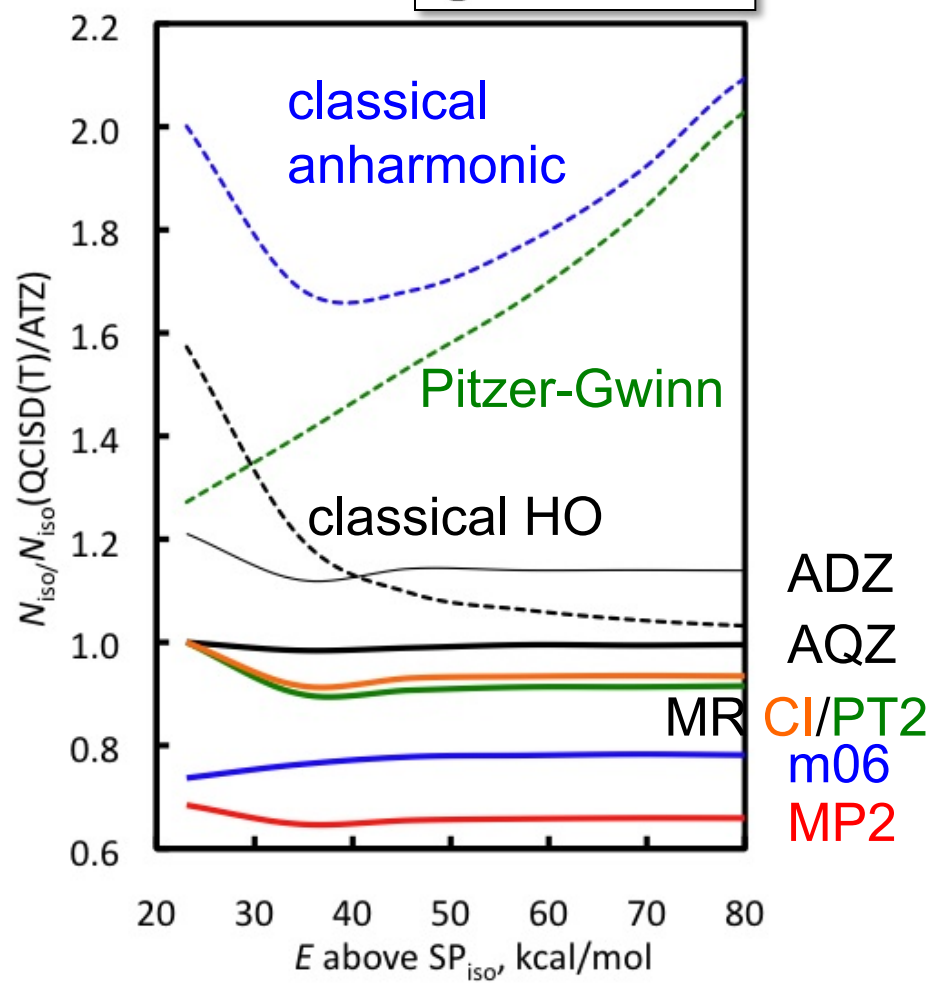



# Counting States: MSXs vs SPs

## Errors due to the PES & the HO model




| | | *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! |



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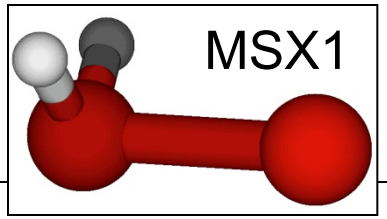
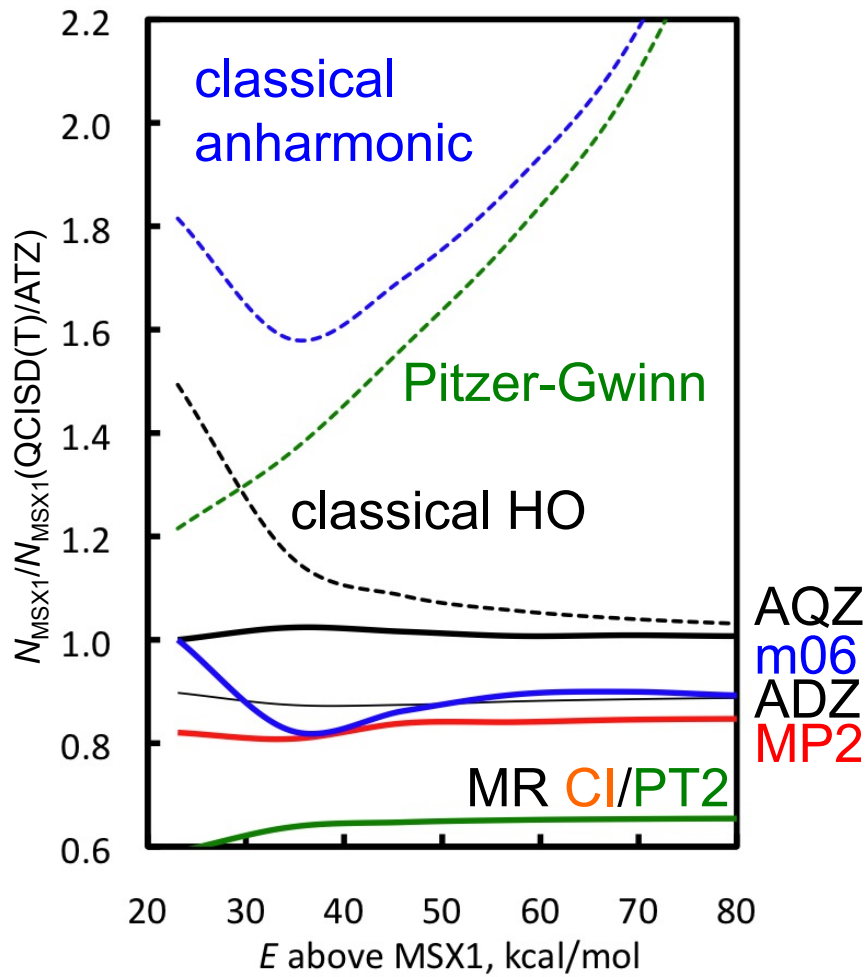



| | | relative to quantal HO QCISD(T)/ATZ | |
|---|---|---|---|
| **quantal HO: basis set** | | | |
| *Beyer-Swinehart direct counts* | ADZ | -15% | small |
| | AQZ | < 2% | |
| **method** | | | |
| | MP2 | -20% | |
| | m06-2x | -10% | |
| | MRCI+Q | -60% ! | big! |
| | CASPT2 | -40% ! | |
| **classical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



# MSX frequencies

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

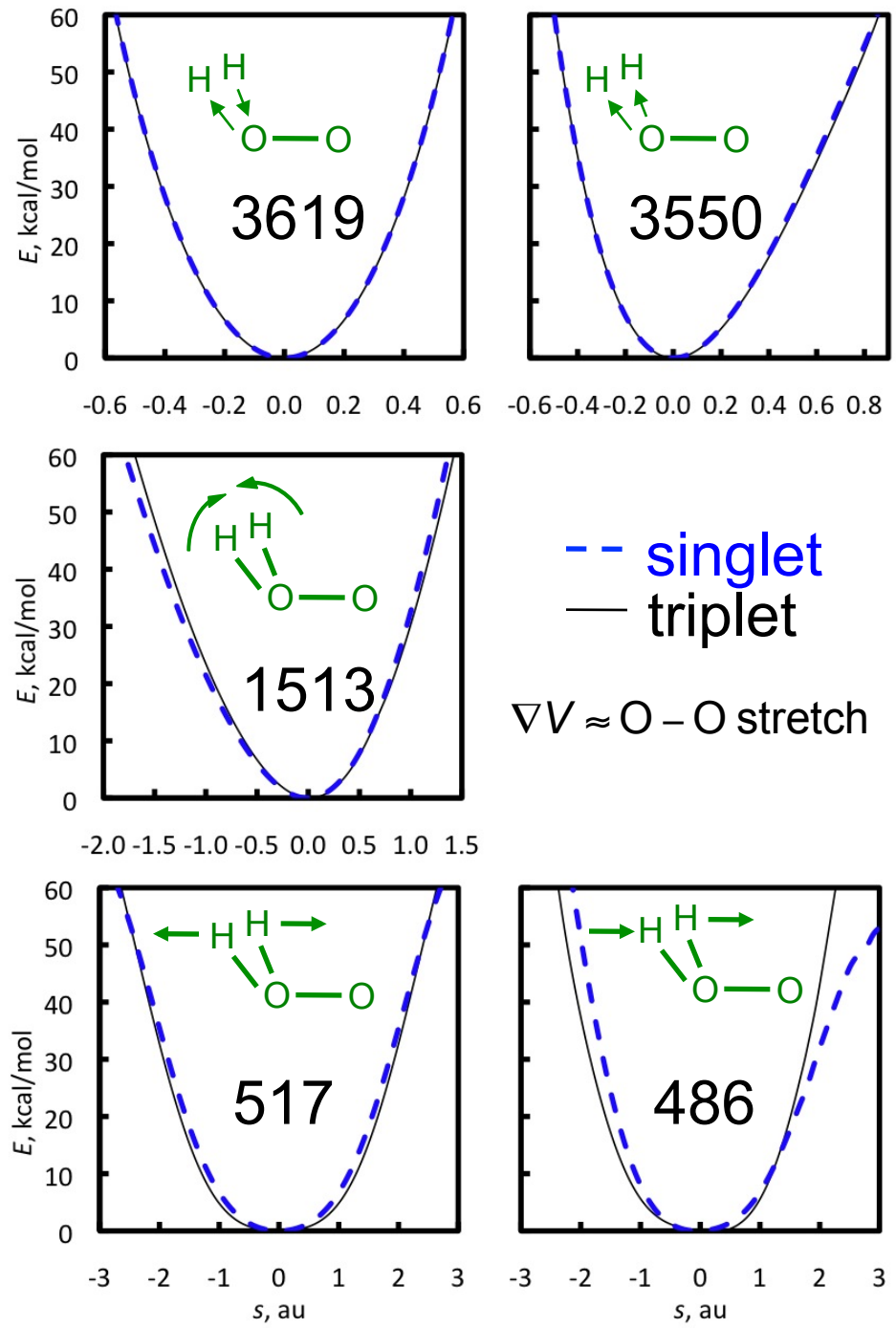
- *frequencies are not invariant to coordinate system*
- *singlet and triplet frequencies do not agree*

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

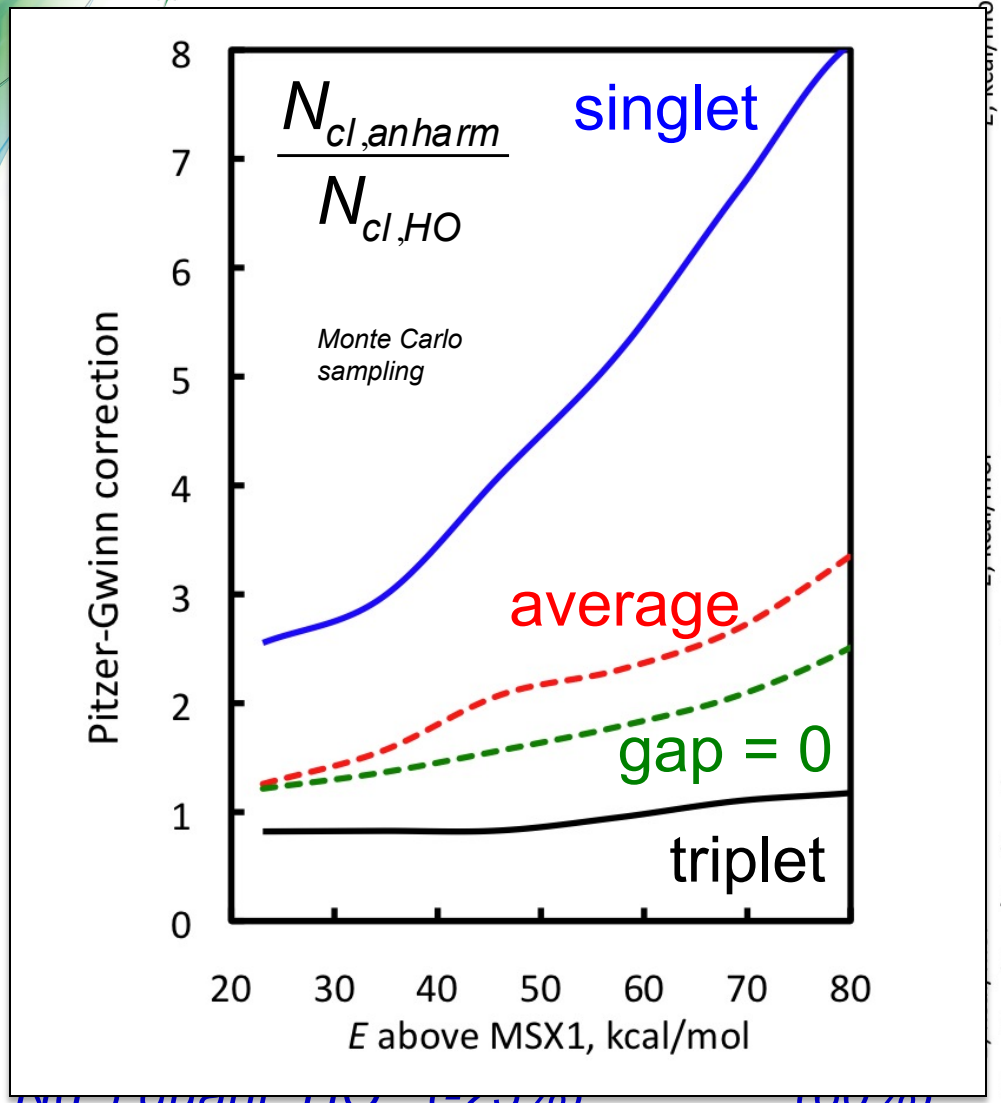
| Average | Singlet | (% diff) | Triplet | (% diff) |
|---|---|---|---|---|
| 486 | 538 | (11) | 430 | (-11) |
| 517 | 571 | (10) | 455 | (-12) |
| 1513 | 1508 | (-0.3) | 1518 | (0.3) |
| 3550 | 3560 | (0.3) | 3541 | (-0.3) |
| 3619 | 3625 | (0.2) | 3612 | (-0.2) |

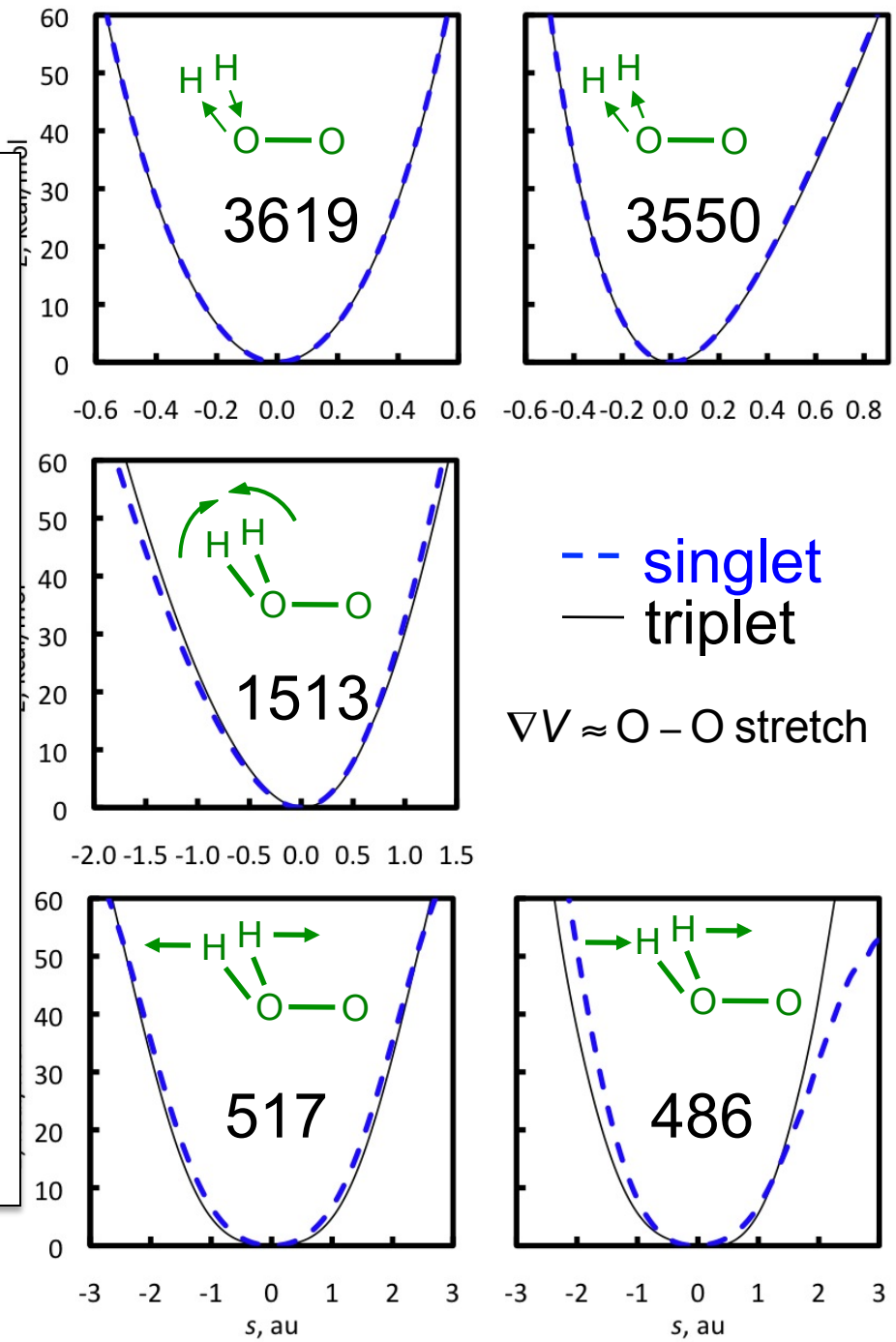
*N(E) quant. HO: (-25%) (60%)*

*Beyer-Swinehart direct counts*



# MSX frequencies




Beyer-Swinehart direct counts

# Errors in spin-forbidden NA "TST" relative to those for spin-allowed TST due to the PES

- Accuracy of the MSX energy is similar to that for saddle point energies
  (not shown, but tested)
- Intrinsic ambiguity in harmonic frequencies at the MSX
  additional error up to 60%
- For anharmonic state counts, finding the true seam is important
  factor of 2-3 error when sampling the "harmonic" seam

**Next: An analysis of errors due to the NA TST model**

# Non-Born-Oppenheimer MD for exploring spin-forbidden physics

NBO MD: full-dimensional semiclassical dynamics

general global electronic couplings

electronic tunneling & (de)coherence

the CSDM variant is the most accurate of the methods tested

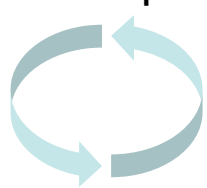
Nuclear d.o.f. (classical)

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

$$\dot{\mathbf{x}} = \mathbf{p} / \mu$$

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

n-e coupling



Electronic d.o.f. (quantal)

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

$$i\hbar \dot{c}_i = \sum_j c_j V_{ij}(t)$$

time-dependent Schrodinger equation

$V_{ij}$ are potentials & couplings

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

# Error analysis for $^3O + CO \rightarrow CO_2$

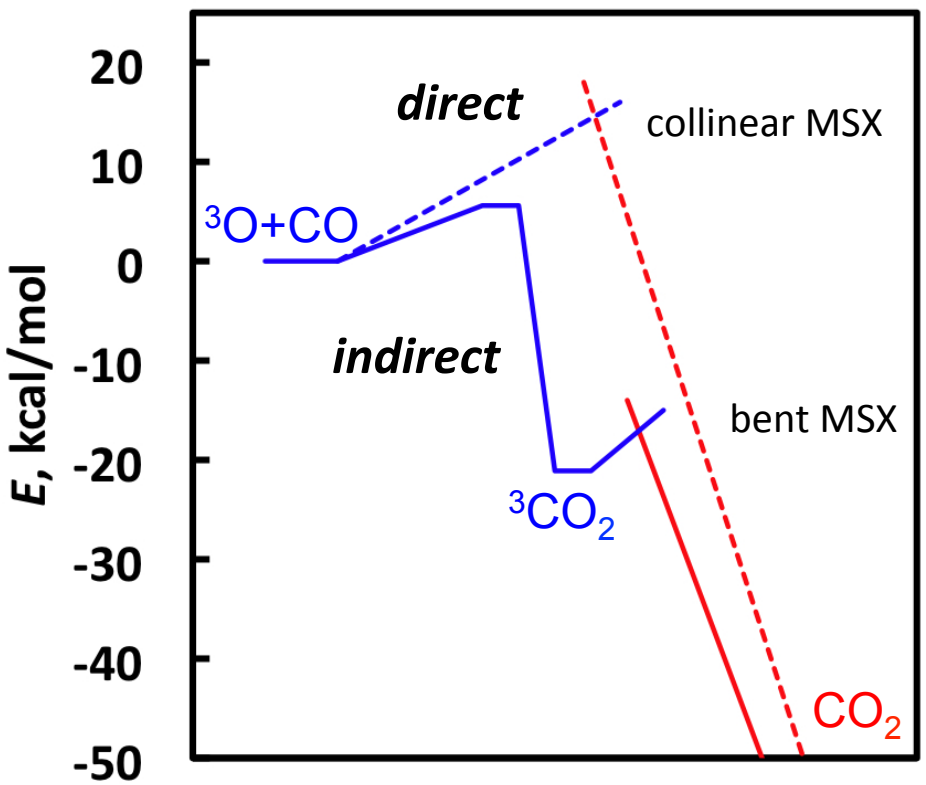
**Competes with CO + OH, etc, to oxidize CO**

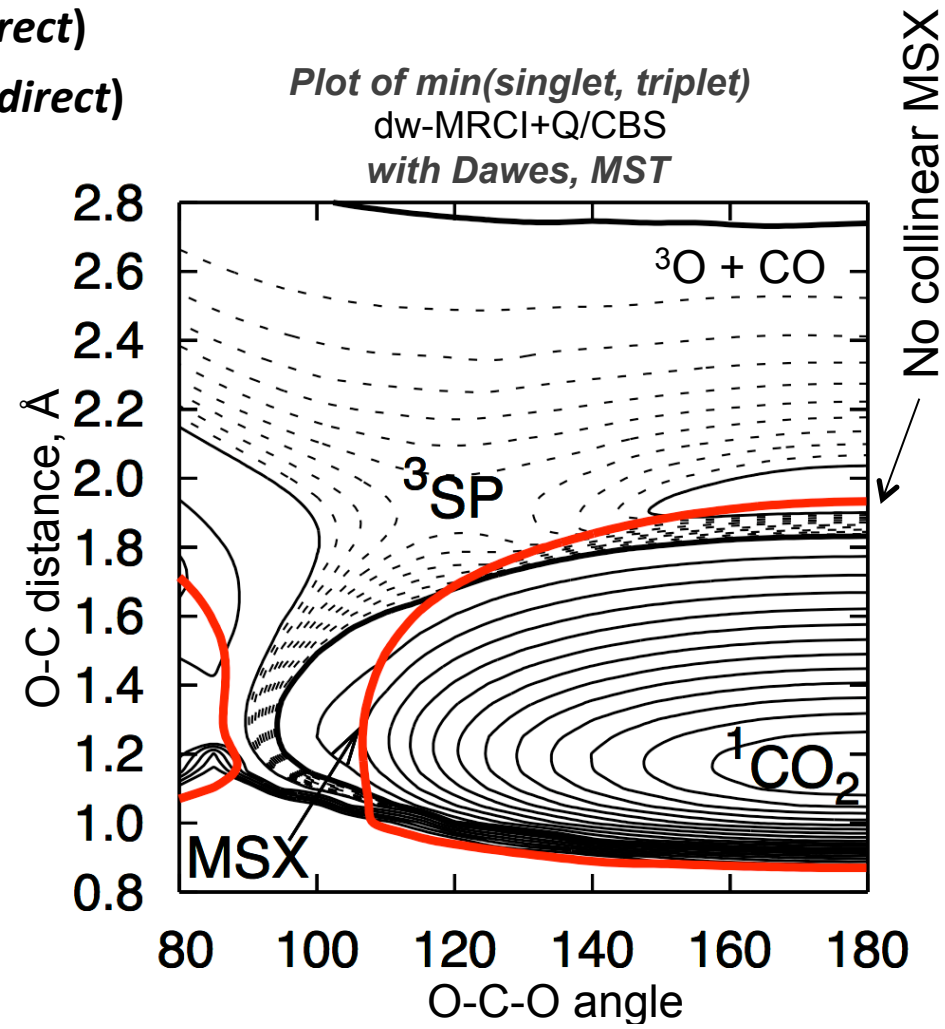
***p*-dependence important in combustion models (Dryer, C&F, 1997; others)**

- No previous ab initio kinetics
- PES characterized (Hwang and Mebel, Chem Phys, 2000)

$^3O + CO \rightarrow$ collinear MSX $\rightarrow CO_2$ (***direct***)

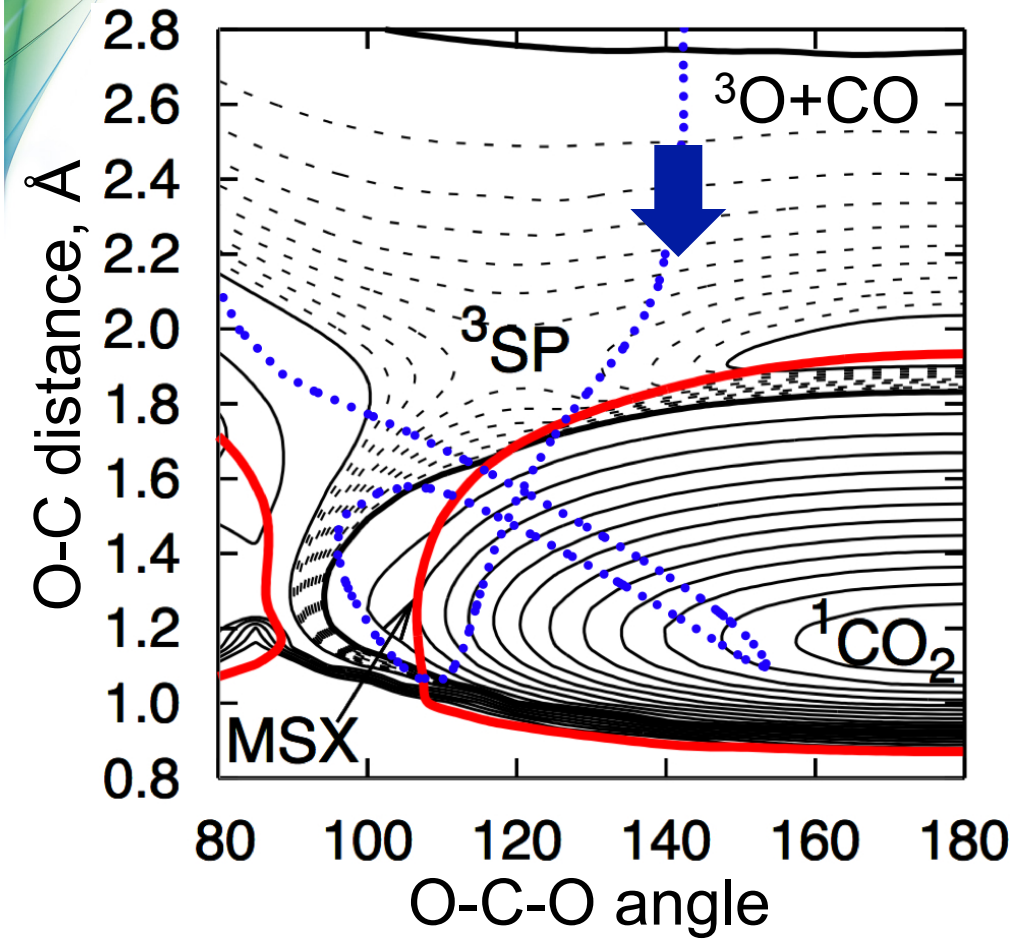
$\rightarrow {}^3CO_2 \rightarrow$ bent MSX $\rightarrow CO_2$ (***indirect***)

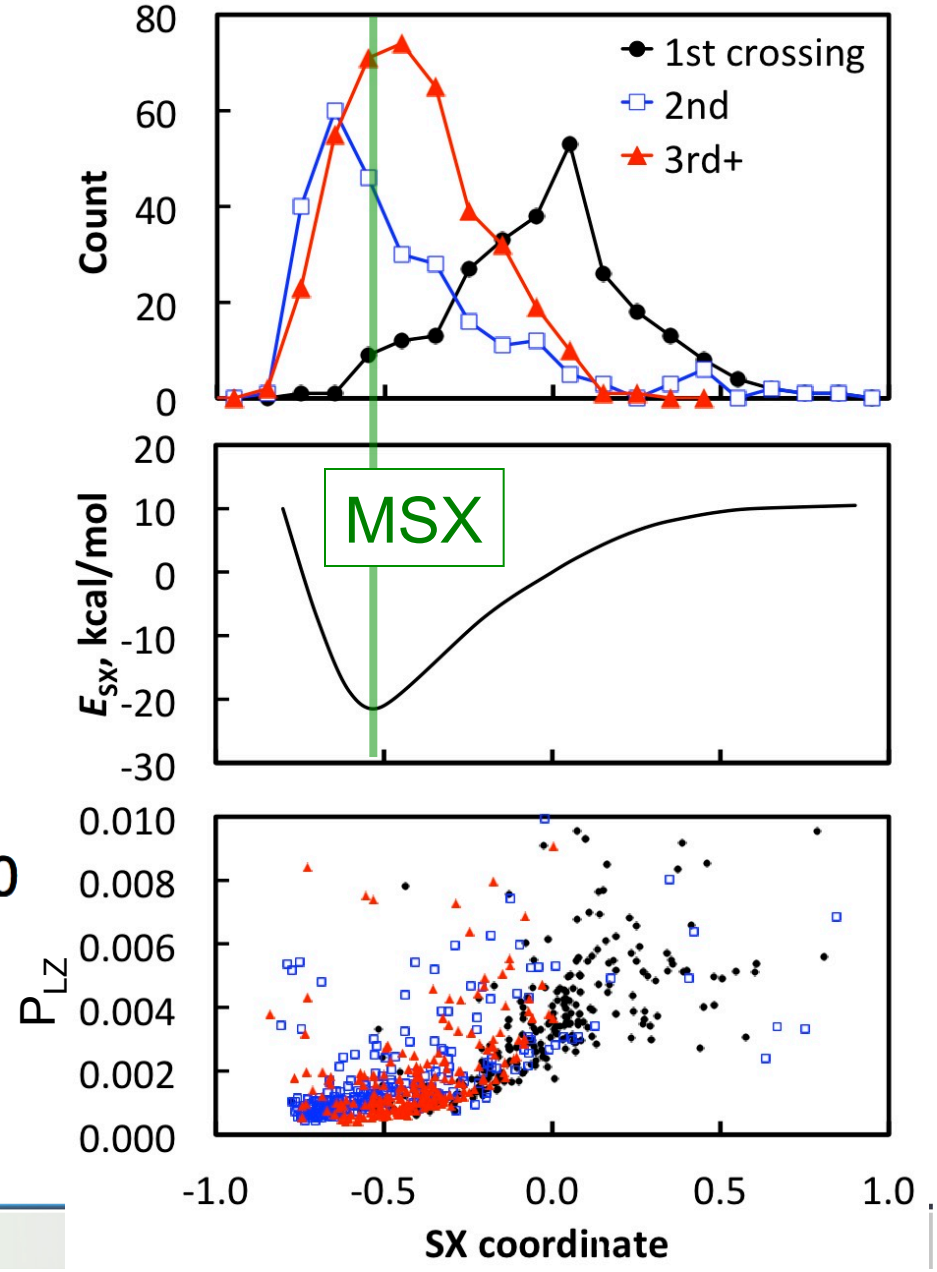


# $^3O + CO$

*min(singlet, triplet)*




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

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

# 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

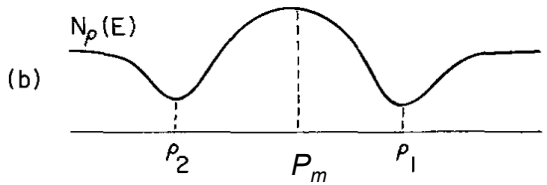



FIG. 5. The flux integral $N_\rho(E)$ through surface $S_\rho$, as a function of $\rho$, for a potential surface of the type in (a) Fig. 1 and (b) Fig. 2.

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

0

statistical

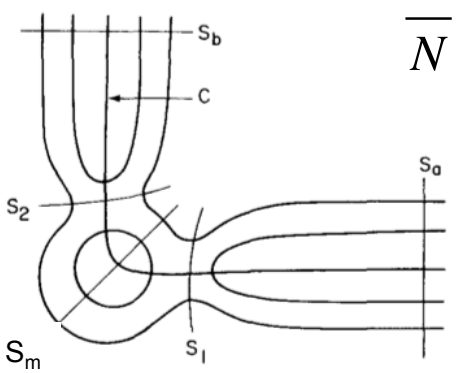
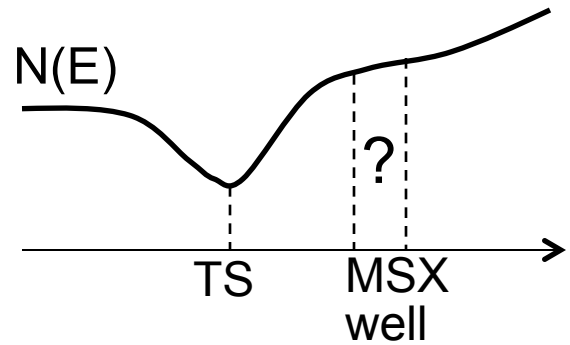
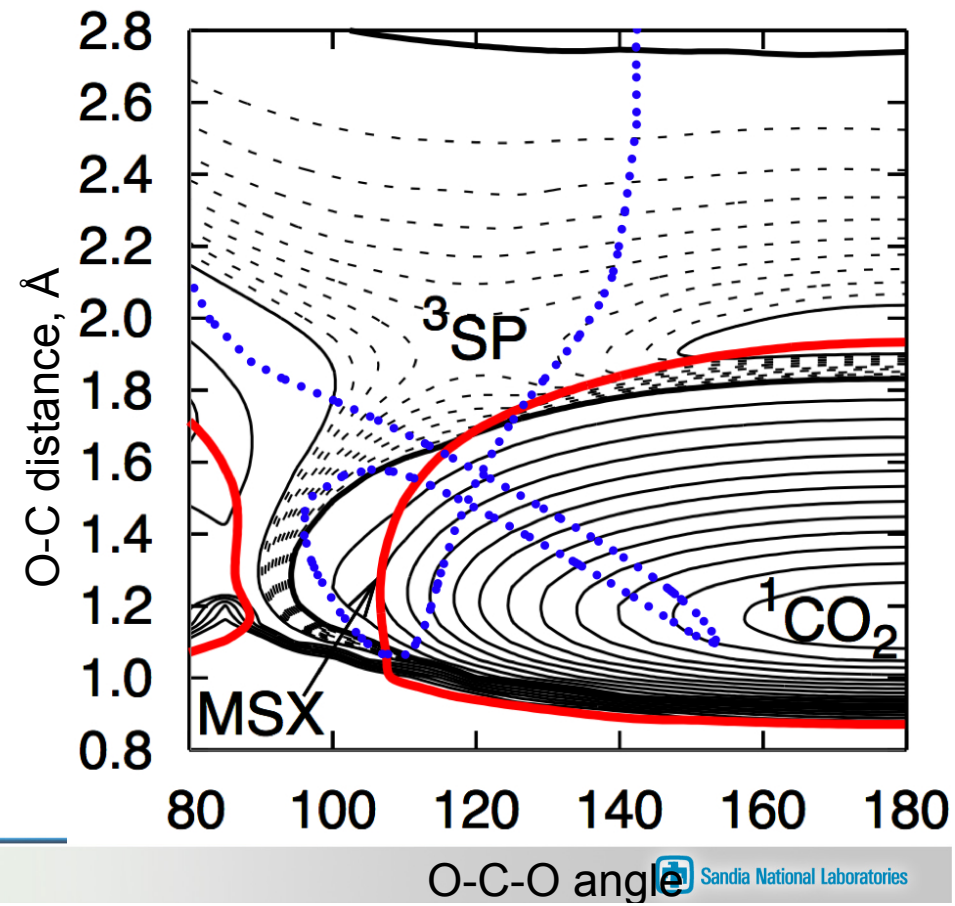



FIG. 2. Sketch of a potential energy surface for a collinear A+BC→AB+C reaction that has an attractive well, corresponding to a stable ABC molecule, that is separated from reactants and products by saddle points. Curve C is the reaction path, and the dividing surfaces $S_1$ and $S_2$ cross it through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



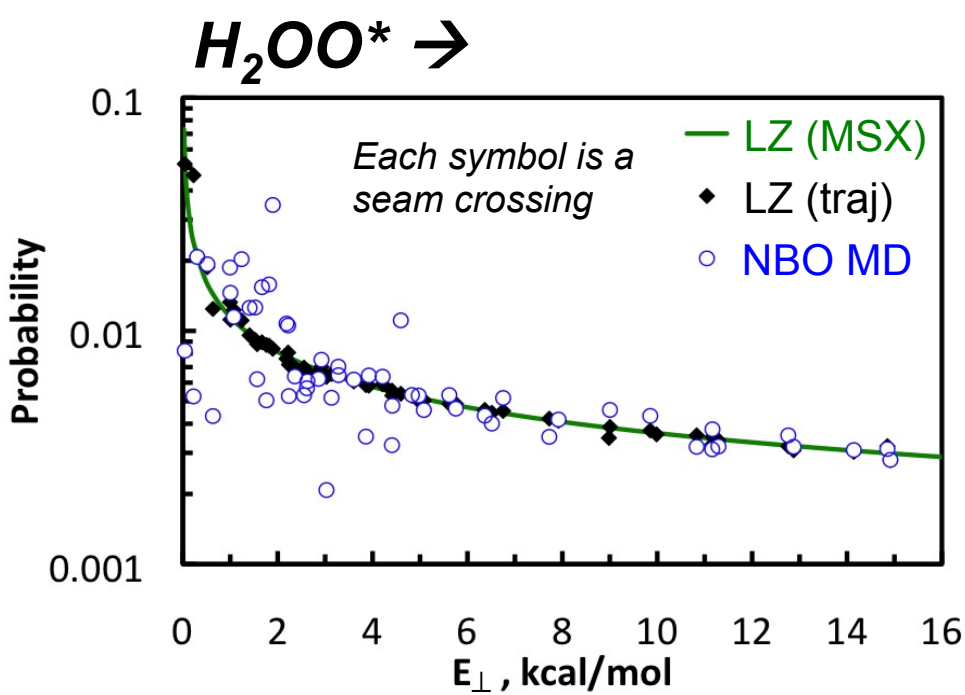



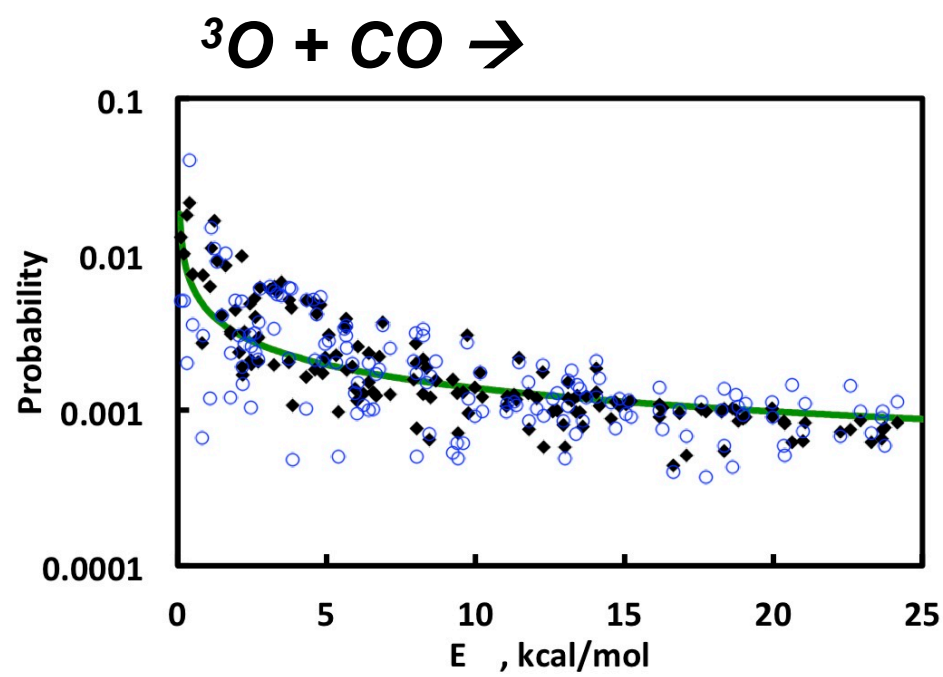
# Multidimensional Effects in $P_{hop}$

Landau-Zener: One-dimensional formula with linear PES & constant $H_{SO}$

Neglects: Geometry dependent spin-orbit seam properties

Multidimensional dynamics




Negligible effect from geometry-dependent seam properties

Up to 3x effect in multidimensional dynamics at low E

Up to 2x from multi-d seam properties

Smaller effect from multi-d dynamics

# Improved spin-forbidden methods

**Direct dynamics CSDM NBO MD**

- Expensive, classical nuclear dynamics

**New statistical theory for spin-forbidden reactions**

- Sample coordinates and momenta on the seam microcanonically

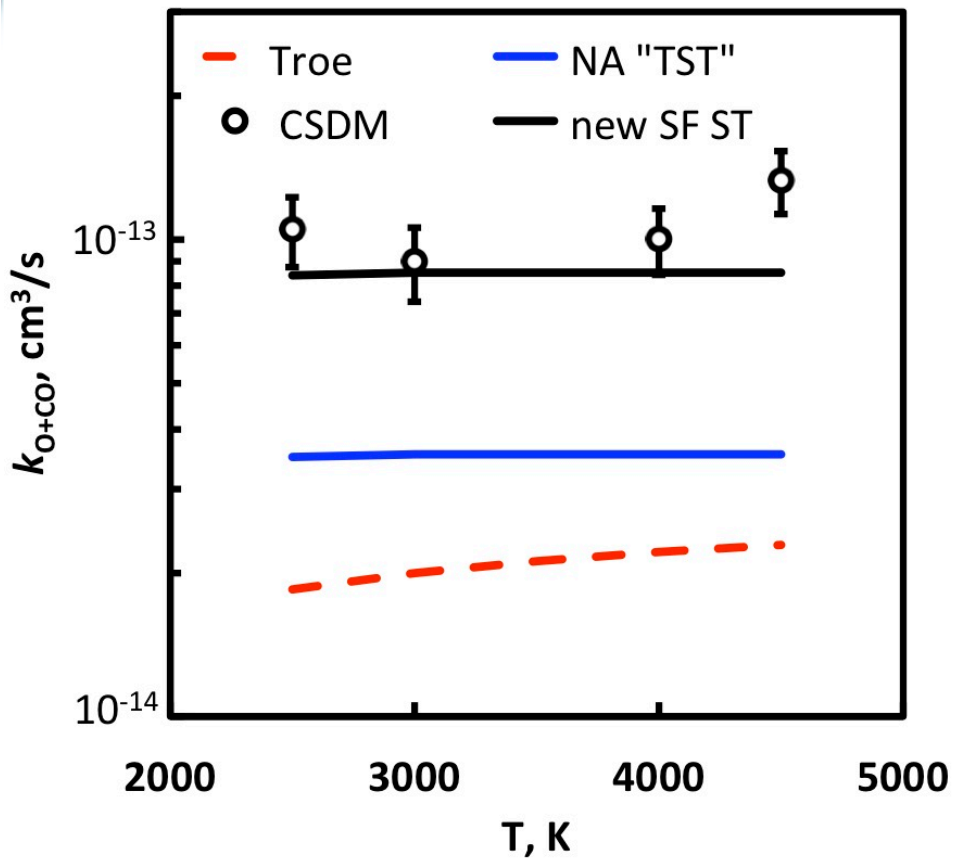
  Anharmonic with shortest-distance gap minimizations

- Multidimensional $P_{hop}$ : Run short-time NBO MD trajectories through seam, $P_{hop}$ (Ex) = $<\rho^f_{11} - \rho^i_{11}>$ ; $\rho^i_{11} = 0$

# Results: O + CO

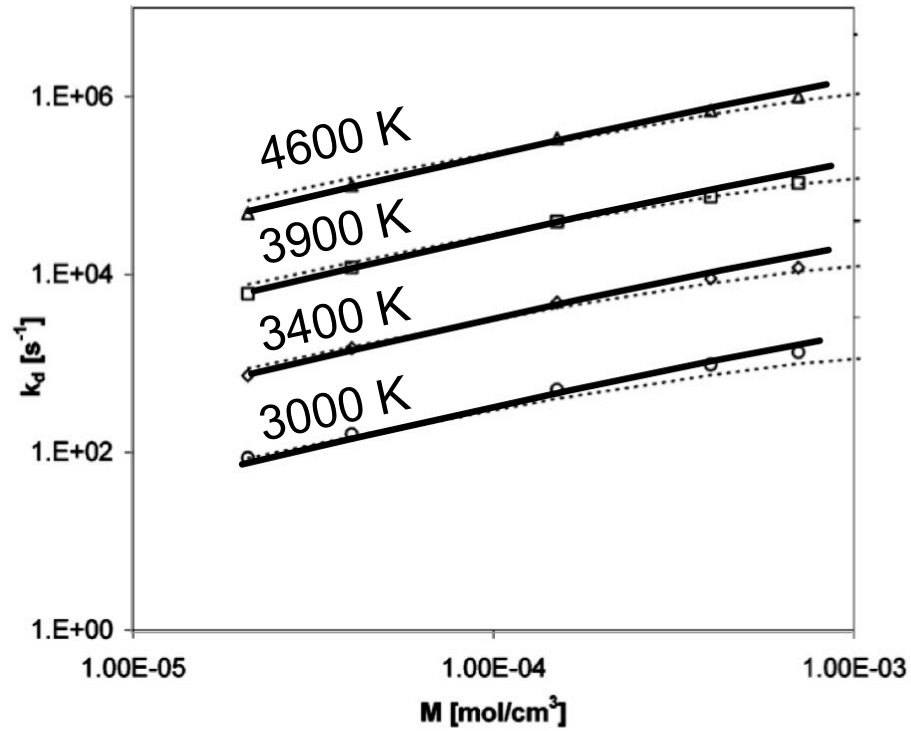
**O + CO high P limit**

**dw-MRCI+Q/CBS**




**$CO_2$ (+ Kr)**

**No falloff at highest exp P (250 atm)**




exp : Wagner, Zabel, Ber. Bunsen-Ges. Phy. Chem. 78, 76 (1974)
analysis : Saxena, Kiefer, Tranter, JPCA 111 3884 (2007)

# Summary

- **Spin-forbidden** kinetics calculations have all the same sources of error as spin-allowed rates **as well as** errors in the simple LZ-based NA "TST" model
- NBO MD (CSDM) can be used to elucidate spin-forbidden physics
- An improved spin-forbidden statistical model incorporates multidimensional hopping probabilities via short-time NBO MD

## Co-workers

**Argonne**
*Larry Harding*
*Stephen Klippenstein*
*Jim Miller*
*Rob Tranter*

**Minnesota**
*Don Truhlar*

**Missouri S&T**
*Richard Dawes*

**Sandia CRF**
*Nils Hansen*
*Eugene Kamarchik*
*Melania Oana*
*Judit Zádor*

# Extra: Crossing seams are not transition states

A crossing seam is not a local minimum in the flux

no variational principle = lots of recrossing

Recrossing is important for nonneglible spin-forbidden rates

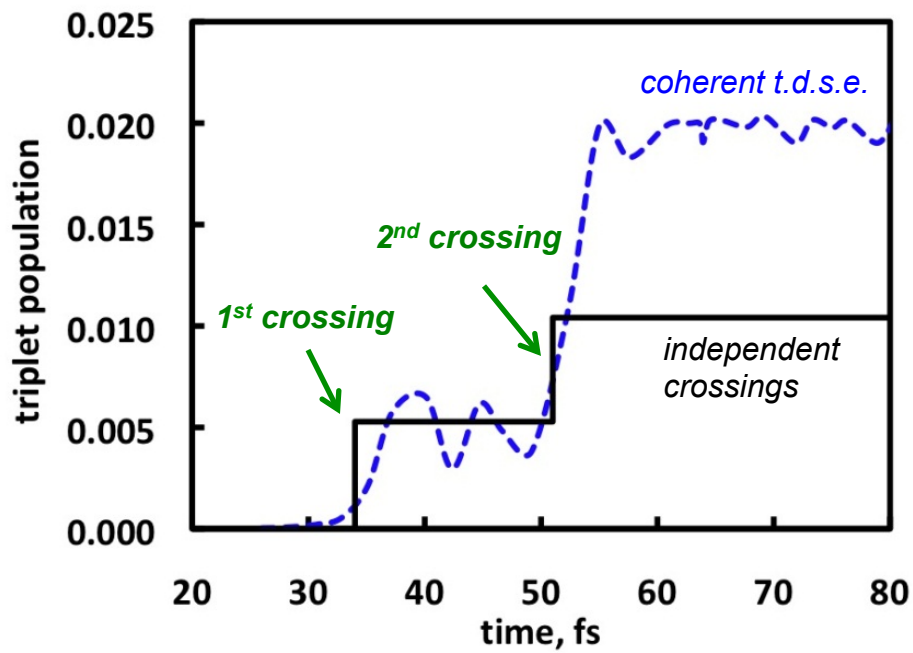
Total SF probability $\approx \sum_{\text{crossings}} P_{\text{hop}}$

**Dynamics is nonlocal only if decoherence is slow**

$\tau_{\text{deco}}$ – time for electronic variables to "reset"

$\Delta t_x$ – time between crossings

Independent 2nd pass if

$\tau_{\text{deco}} < \Delta t_x$

*Electronic dynamics along a trajectory*