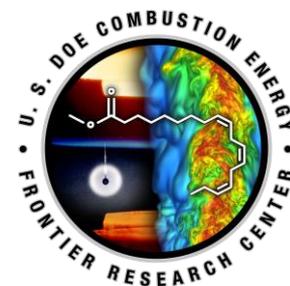




August 17, 2011 CEFRC Annual Meeting



Computation of accurate thermochemistry and rate parameters for complex combustion reactions

Donald G. Truhlar

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John
Alecu

Steven
Mielke

Ewa
Papajak

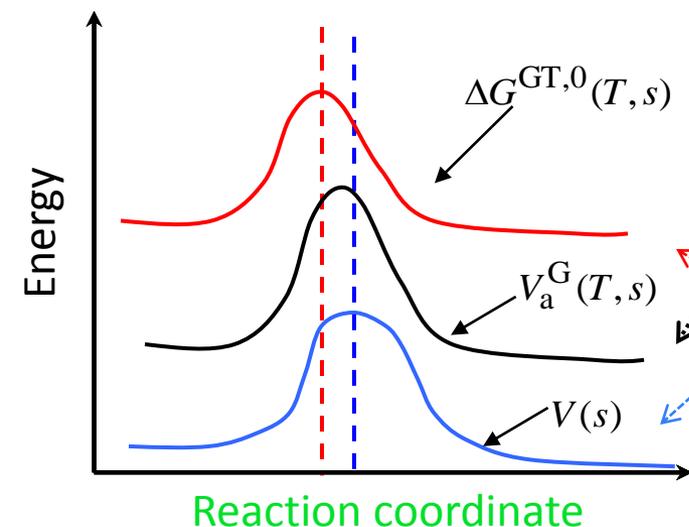
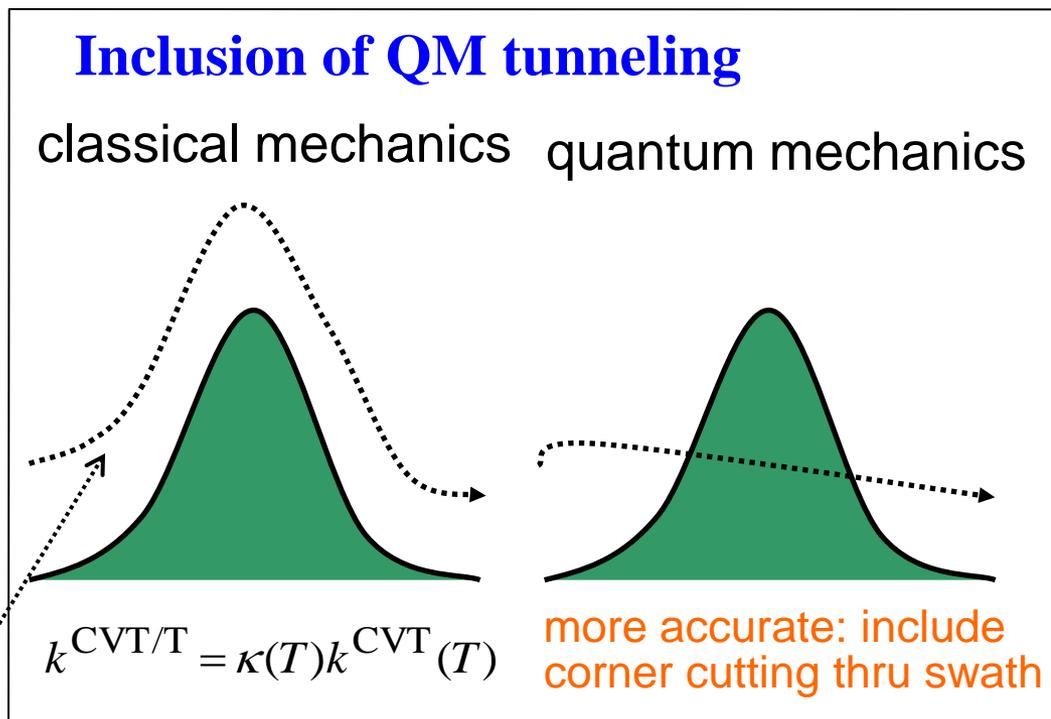
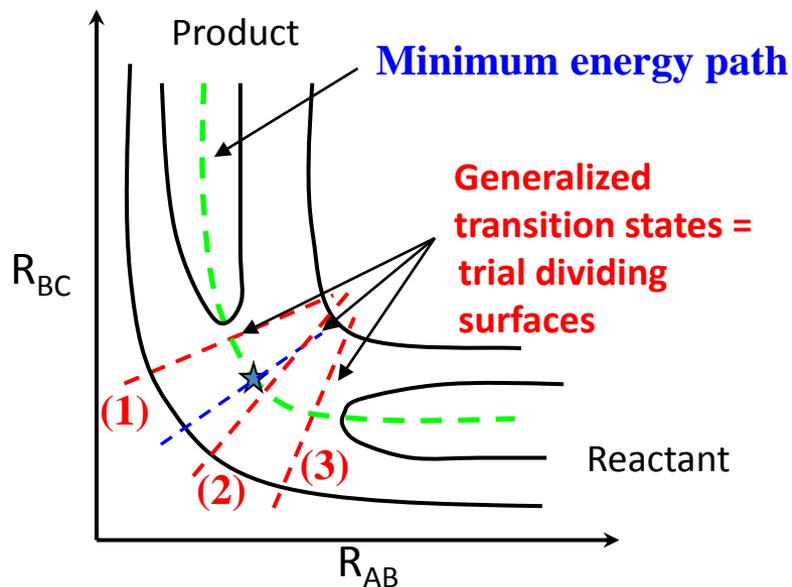
Prasenji
Seal

Xuefei
Xu

Tao
Yu

Jingjing
Zheng

Variational transition state theory (VTST) with multidimensional tunneling corrections



Conventional TS:

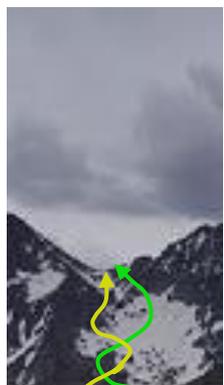
at **Potential Energy** max.

Variational TS: at **Free energy** max.

$$k^{CVT} \leftrightarrow \max_s \Delta G^{GT,0}(T,s)$$

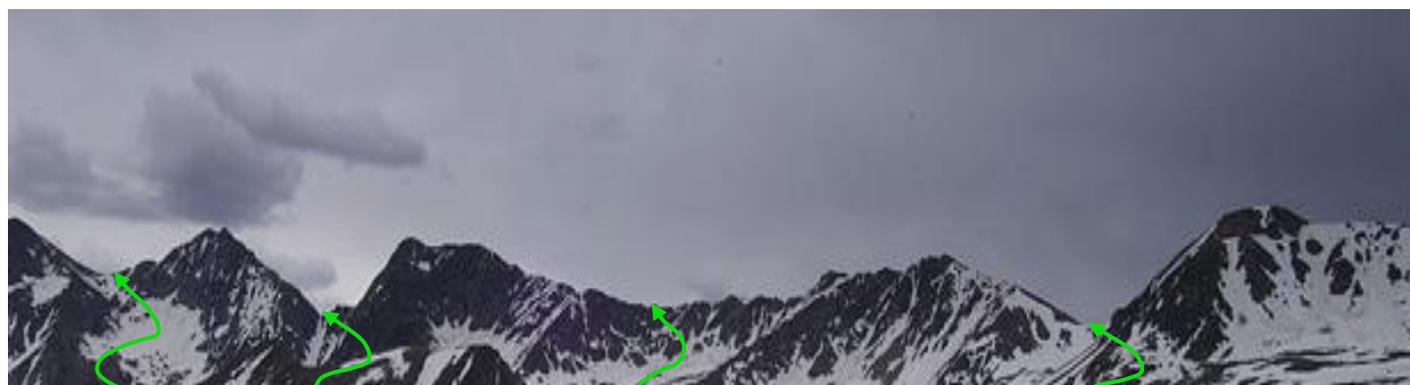
many paths over the mountain

Textbook
case;



reactant

For complex molecules, there is an ensemble of reaction valleys and saddle points (Often connected by torsions)



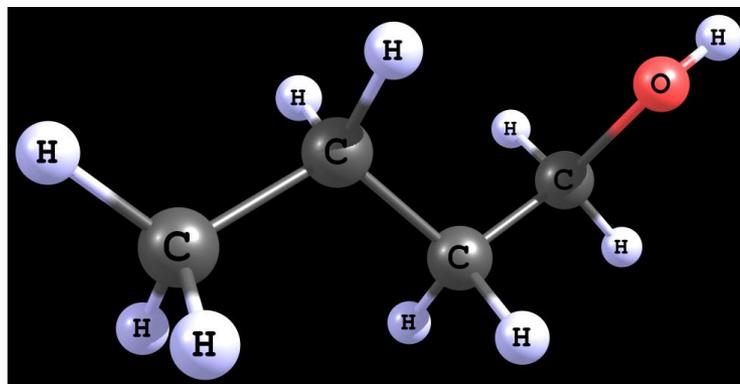
reactant

We ensemble average over these valleys; each has its own reaction coordinate.

Example:

n-Butanol + Hydroperoxyl Radical

Reactant has
36 structures.



Transition state has
136 structures.

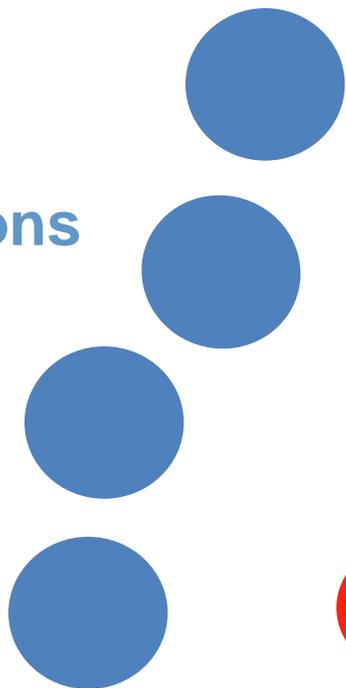


Product radical has 29 structures.

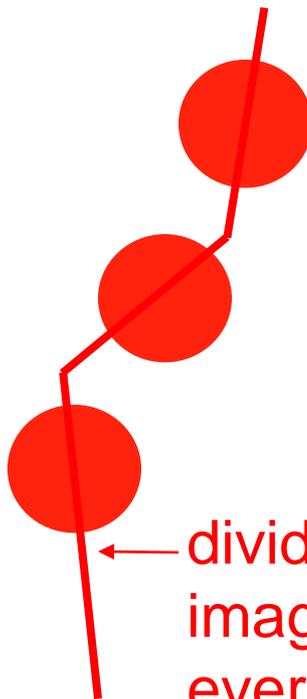
Multi-structural VTST: a multi-faceted dividing surface

configuration space

Reactant conformations



do not need information about the region half way up the hill, except to calculate tunneling

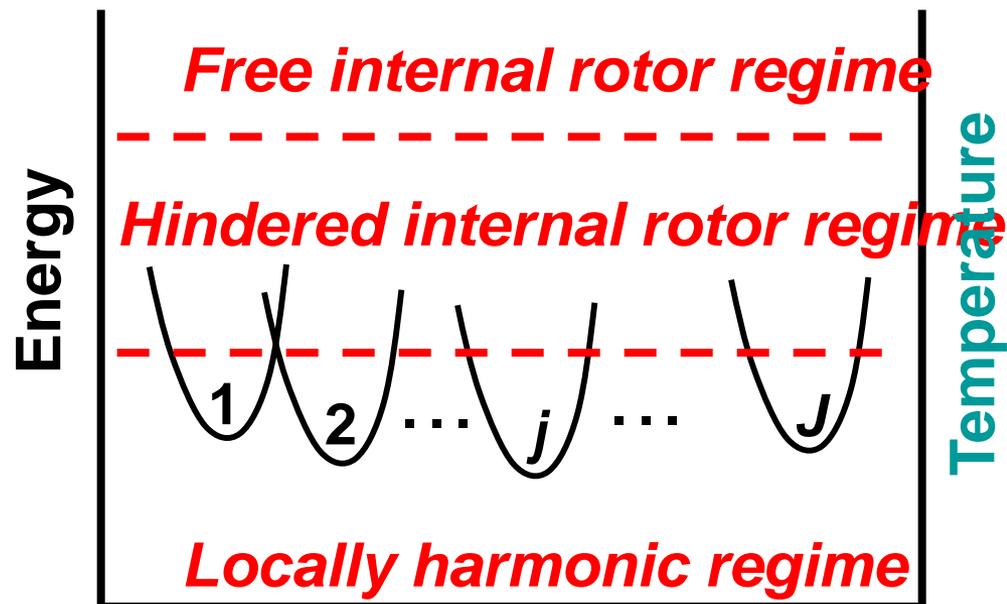


Product region on this side of dividing surface

dividing surface orthogonal to imaginary-frequency normal mode of every transition state conformation – calculate free energy of activation for this multi-faceted surface

But the dividing surfaces are not independent,
except maybe at low T .

Transition state conformers:

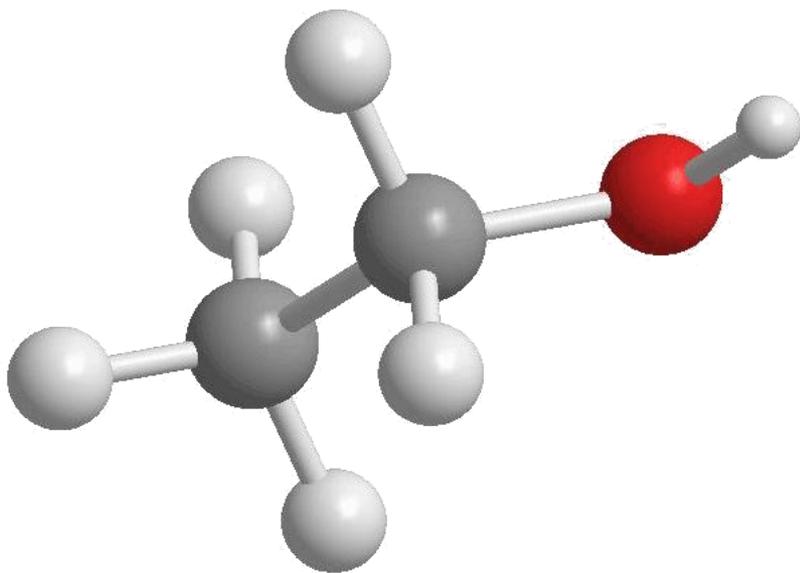


Similarly the reactant conformational regions overlap
when available energy exceeds torsional barriers.

Another complication:

One cannot just substitute a torsion partition function for a normal mode harmonic one.

Torsions are mixed with each other and with other low-frequency normal modes.



Example: ethanol.

Low-frequency normal modes are symmetric and antisymmetric combinations of the 2 torsions.

Torsions are not separable. Examples.

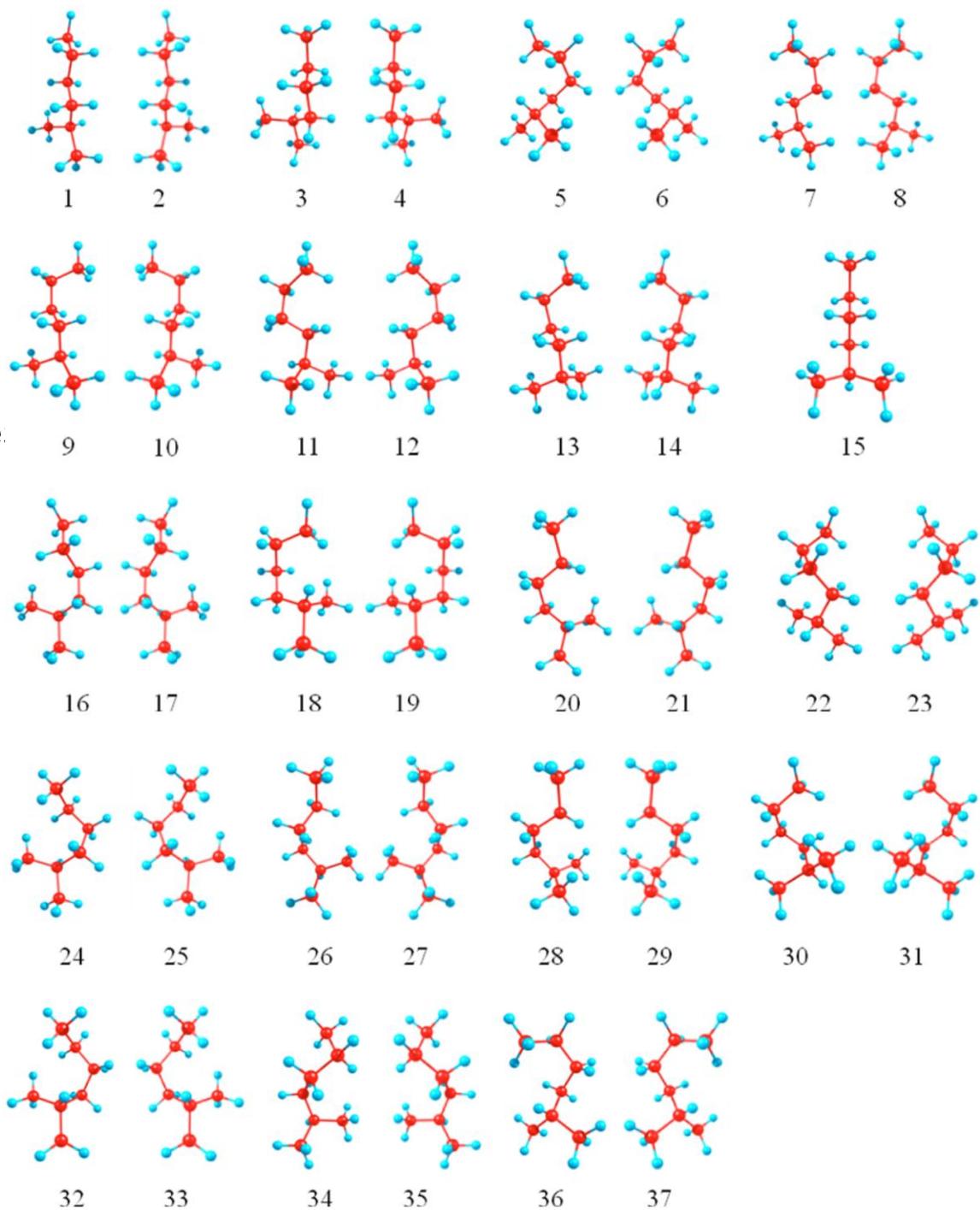
Isoheptane, if separable, would have $3^3 = 27$ structures

We find 37, shown at right:

Notice that structures 1–14 and 16–37 occur in mirror image pairs.

n-Heptane, if separable, would have $3^4 = 81$ structures.

We find 59.



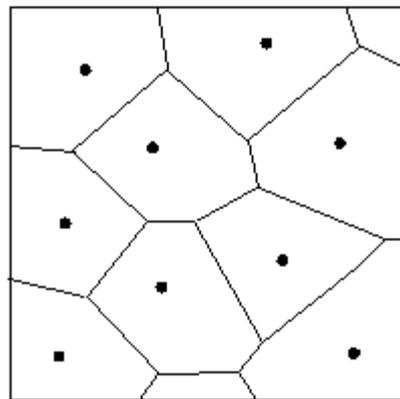
Computer program for including torsional anharmonicity in thermochemical calculations on complex molecules

We proposed a new approximation called

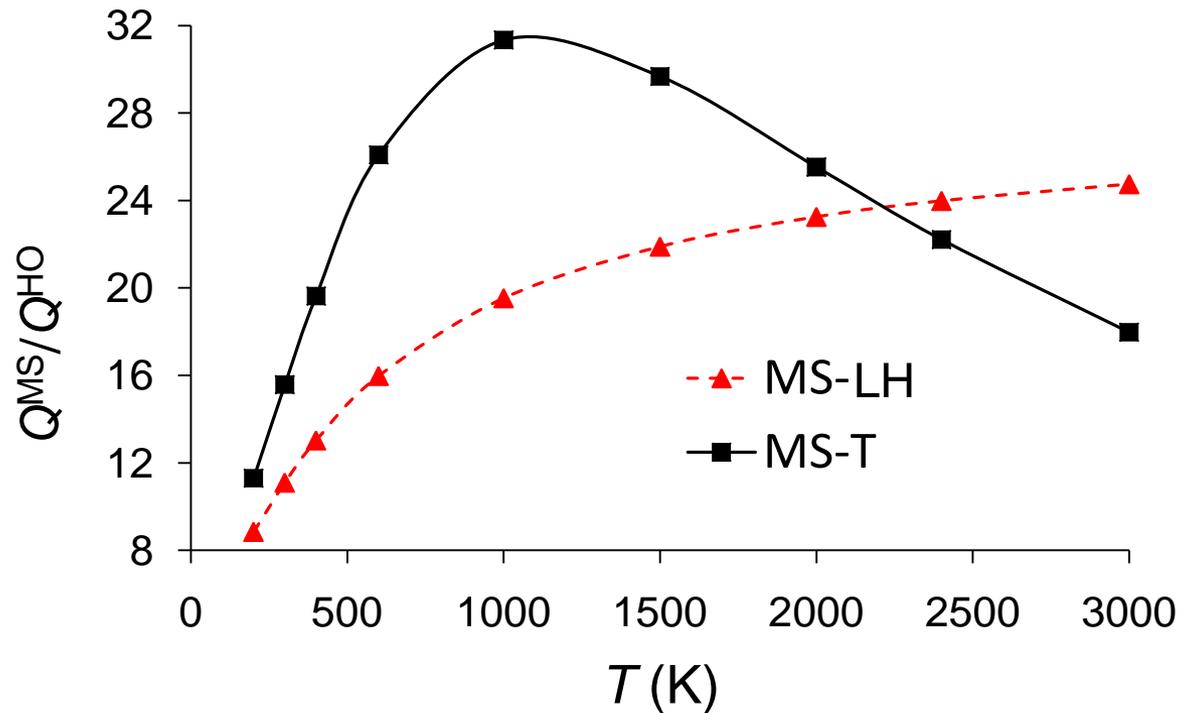
multi-structural method including torsional anharmonicity (MS-T)

to calculate conformational-vibrational-rotational partition function.

- Applicable to molecules with multiple torsions coupled with each other or with other low-frequency modes
- Assigning torsions to specific normal modes is not required or assumed.
- Low computational cost—need not optimize or even find torsional barriers—instead implicitly account for their height from Voronoi volumes of stable structures in torsion angle space



Partition function of butanol



Ratio of the conformational-rovibrational partition function calculated by the multi-structural method (29 structures) to that calculated by the single-structure local harmonic approximation at the global minimum.

PES: MPW1K/6-311+G(2df,2p)

Entropy of *n*-butanol

$$S = k_B \ln Q - \frac{1}{T} \left(\frac{\partial \ln Q}{\partial \beta} \right)_V \quad (\text{cal mol}^{-1} \text{ K}^{-1})$$

T (K)	SS-HO	MS-T	Group Additive (empirical)	Direct experiment
298	80.0	87.2	85.9	86.8 ^a
400	88.5	96.1	94.6	
1000	131.3	138.1	136.5	

^a J. F. Counsell, J. L. Hales, and J. F. Martin, Trans. Faraday Soc. **61**, 1869 (1965).

etc. – successful comparisons to
API data, TRC data, other empirical and experimental data
for ethanol, hexane, isohexane, heptane, isoheptane.

But we can do radicals, transition states, and molecules for
which experimental data is not available.

A practical approach to compute the rate constant

$$k = \kappa^G(T) \frac{\tilde{k}T}{h} \min_s \frac{Q_1^{\text{GT,HO}}(T,s) \frac{Q_{\text{con-rovib}}^{\ddagger,\text{MS-T}}(T)}{Q_1^{\ddagger,\text{HO}}(T)}}{Q_{\text{con-rovib}}^{R,\text{MS-T}}} \exp(-V(s)/\tilde{k}T)$$

separable multi-structure
anharmonicity factor

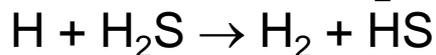
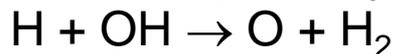
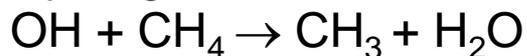
Reaction path calculations for variational effects and tunneling

Semi-direct dynamics by Multi-Configuration Shepard Interpolation:

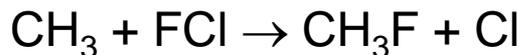
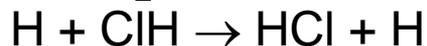
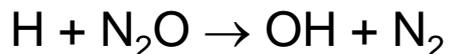
- semiautomatic interpolation aided by molecular mechanics
- ~9 Shepard-points (energy, gradient, Hessian)

Transition state geometry database

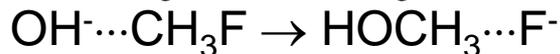
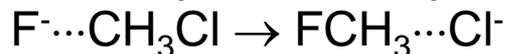
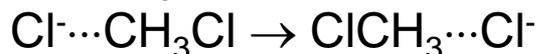
Hydrogen transfer



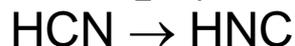
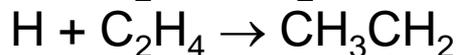
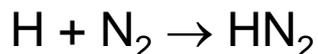
Heavy-atom transfer



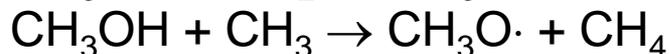
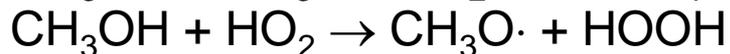
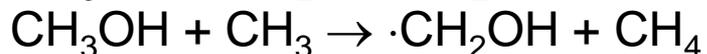
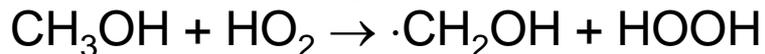
Nucleophilic substitution of anion



Unimolecular and association



Methanol hydrogen transfer



Mean unsigned errors (Å) in active internuclear distances* at saddle points

*those involved in bond formation and bond breaking

Density functional theory with MG3S basis set

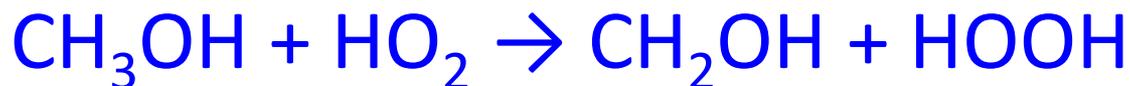
M08-HX	0.014
M06-2X	0.017
M08-SO	0.021

factor of ~4 improvement
over B3LYP

B3LYP	0.065
BLYP	0.123

Wave function theory with MG3S basis set

QCISD	0.015
MP2	0.037



compare energetics to Klippenstein, Harding, Davis, Tomlin, Skodje 2011

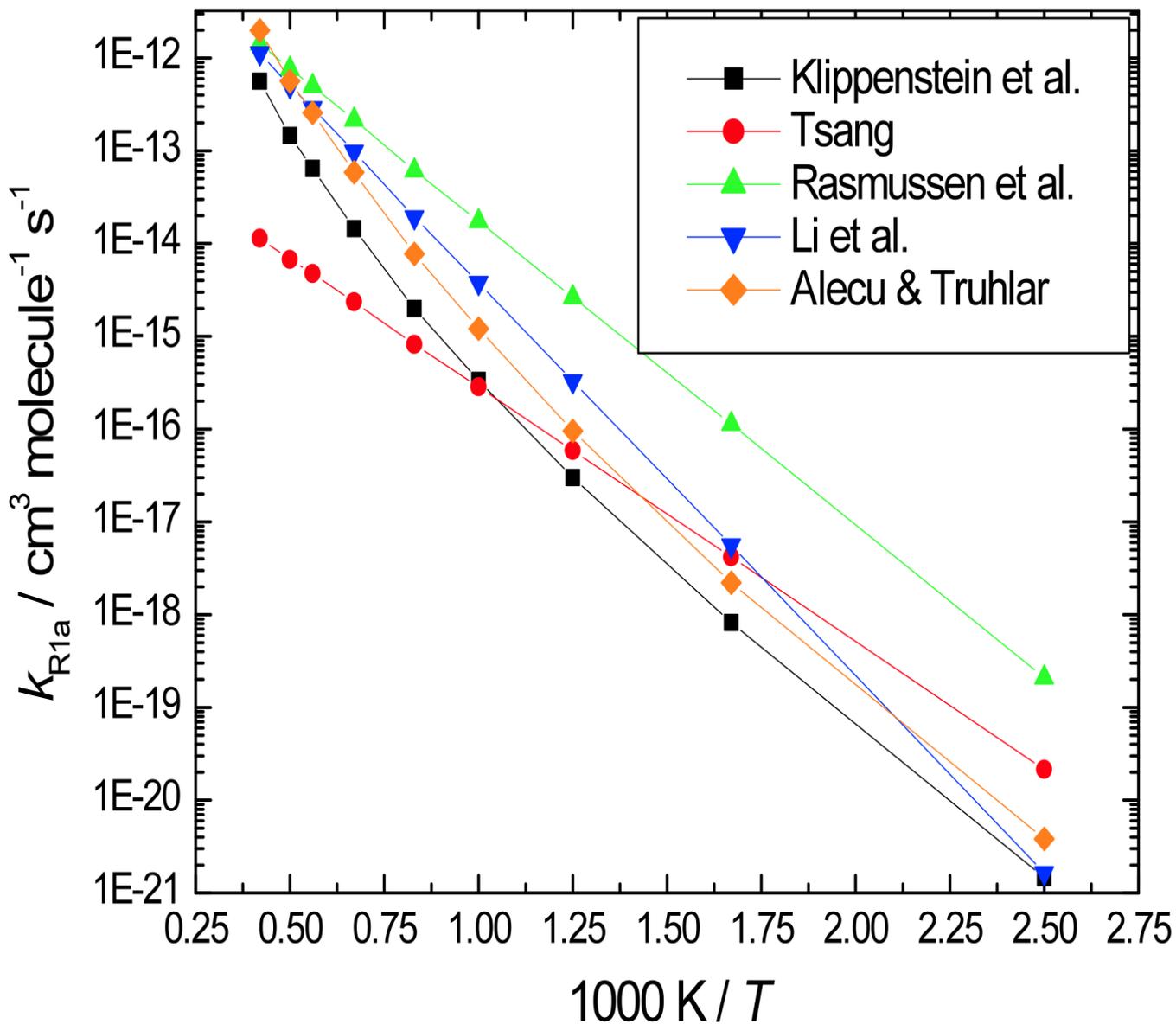
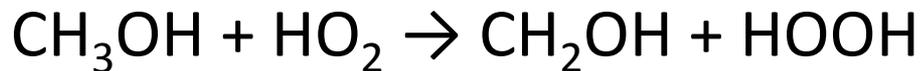
	ΔH_0	ΔH_0^\ddagger	
Klippenstein et al.	8.26	15.27	kcal/mol
present			
—CCSDT(2) _Q /CBS	8.26	15.40	
—DFT used for kinetics	8.36	15.46	

multi-structural-torsional anharmonicity factors, 300 to 2400 K

reactant	1.2 to 0.7
transition state	1.8 to 11.3

multi-dimensional tunneling transmission coefficients, 300 to 1000 K

small-curvature	66 to 1.4
microcanonically optimized	82 to 1.4



differences from previous:

Rasmussen et al. 2008
> factor of 50

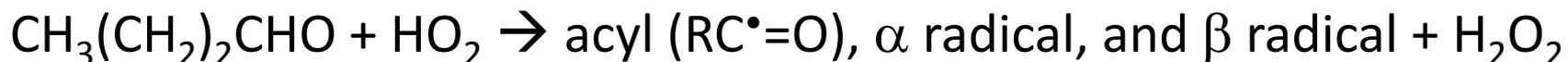
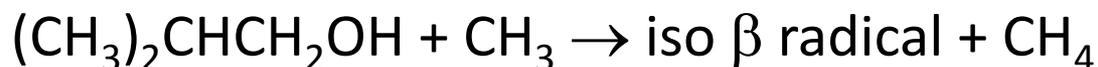
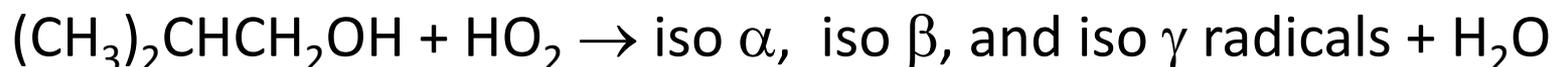
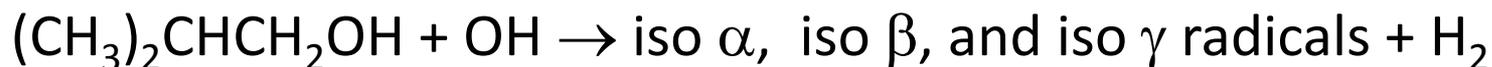
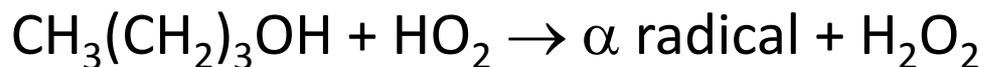
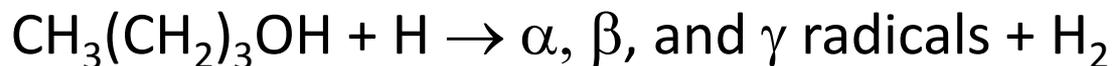
Tsang 1987
> factor of 10

Klippenstein et al. 2011
factors of 2.6-4

Li, Dryer et al. 2007
< factor of 3.4

Quick summary of work in progress on butanol and butanal reactions

Work is in progress on all of the following 18 reactions:



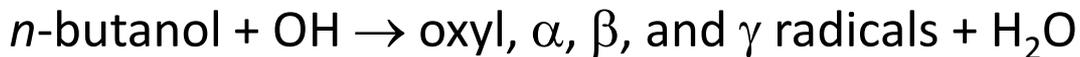
butanol and butanal (continued)

Our strategy is essentially the same for all reactions:

- (1) Validate a DFT method, usually M08-HX or M08-SO, against higher-level calculations, usually CCSD(T).
- (2) Find all structures (conformers) of the reactants, transition state, and products by DFT optimizations; calculate frequencies for all structures.
- (3) Create a multi-configuration Shepard interpolation (MCSI) of the dominant reaction path and use it for variational transition state and multidimensional tunneling calculations.
- (4) Include multi-structural torsional anharmonicity for all structures by the MS-T method to obtain the final MS-VTST rate constants including multi-dimensional tunneling. (The reactions with OH require additional considerations because the reaction barrier is low compared to barriers for interconverting conformers of the reactant.)

In most cases, steps (1) and (2) are done; steps (3) and (4) are in progress.

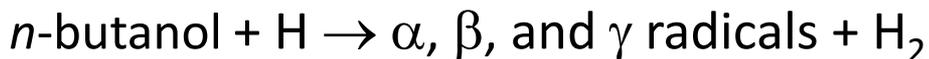
Summary of structures found



reactant structures: 29

TS structures: 110, 74, 98, and 78

product structures: 29, 36, 38, and 36



TS structures: 26, 42, and 44



TS structures: 136



reactant structures: 9

TS structures: 20, 18, and 100

product structures: 12, 8, and 18



TS structures: 74, 52, and 250



TS structures: 12



reactant structures: 29

TS structures: 110, 74, 98, and 78

product structures: 29, 36, 38, and 36

Sample results

barrier heights (kcal/mol)

isobutanol + OH

	M08-HX/6-311+G(2df,2p)	CCSD(T)-F12a/jun-cc-pVTZ
α	-0.6	-0.5
β	-1.4	-1.6
γ	0.6	0.7

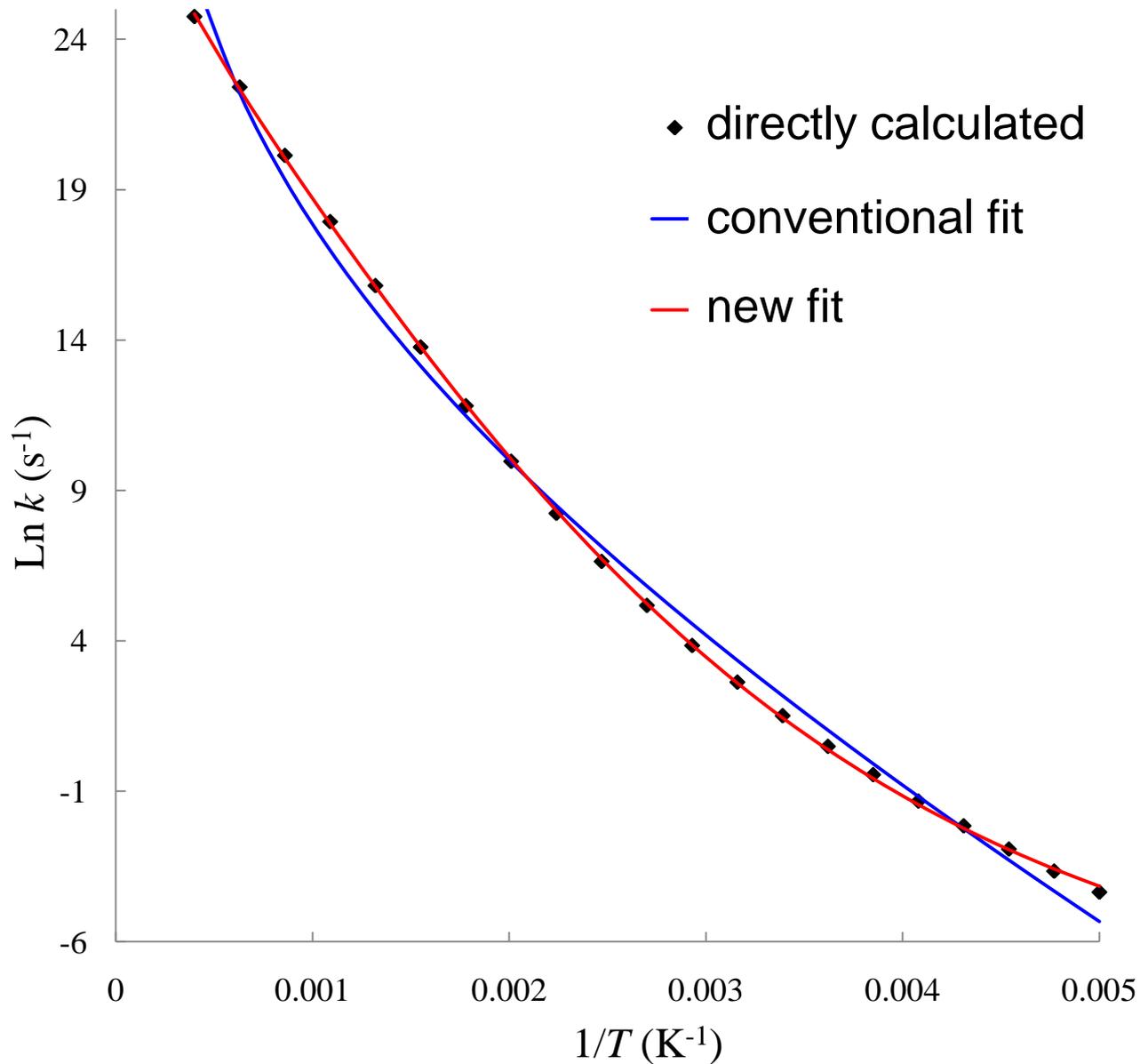
rate constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

n-butanol + HO₂ → α radical + H₂O₂ (barrier = 14.0 kcal/mol)

MS-VTST/SCT:M08-SO/MG3S:MCSI-6

1000 K 6.80×10^{-16}

Hydrogen-transfer isomerization of butoxyl



Rate expression

$$k = A \left(\frac{T}{300 \text{ K}} \right)^n \exp(-E / RT)$$



Energy of activation

$$E_a = E + nRT$$

$$k = A \left(\frac{T}{300 \text{ K}} \right)^n \exp \left(- \frac{E(T + T_0)}{R(T^2 + T_0^2)} \right)$$



$$E_a = E \frac{T^4 + 2T_0T^3 - T_0^2T^2}{(T^2 + T_0^2)^2} + nRT$$

E_a (kcal/mol) for 1, 4-hydrogen shift isomerization of 1-pentyl radical

T	300	400	600	1000	1500
new fit	12.6	15.6	18.7	21.7	23.4
linear in T	12.6	13.5	15.3	18.9	23.4