

Annual Report  
**Combustion Energy  
Frontier Research Center**

Princeton, NJ  
Sept. 23, 2010

**Truhlar group  
University of Minnesota**



John  
Alecu



Steven  
Mielke



Ewa  
Papajak



Xuefei  
Xu



Tao  
Yu



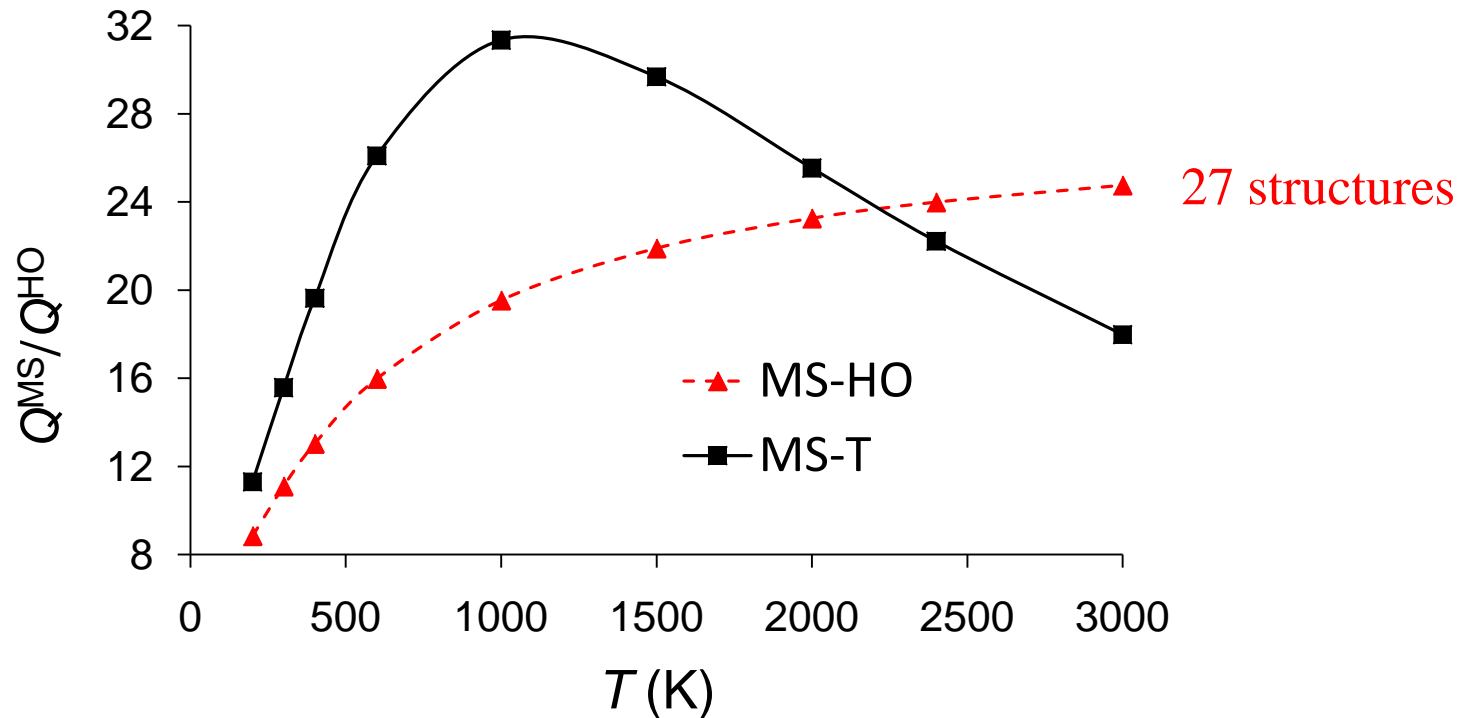
Jingjing  
Zheng

# Practical methods for including torsional anharmonicity in thermochemical calculations on complex molecules

---

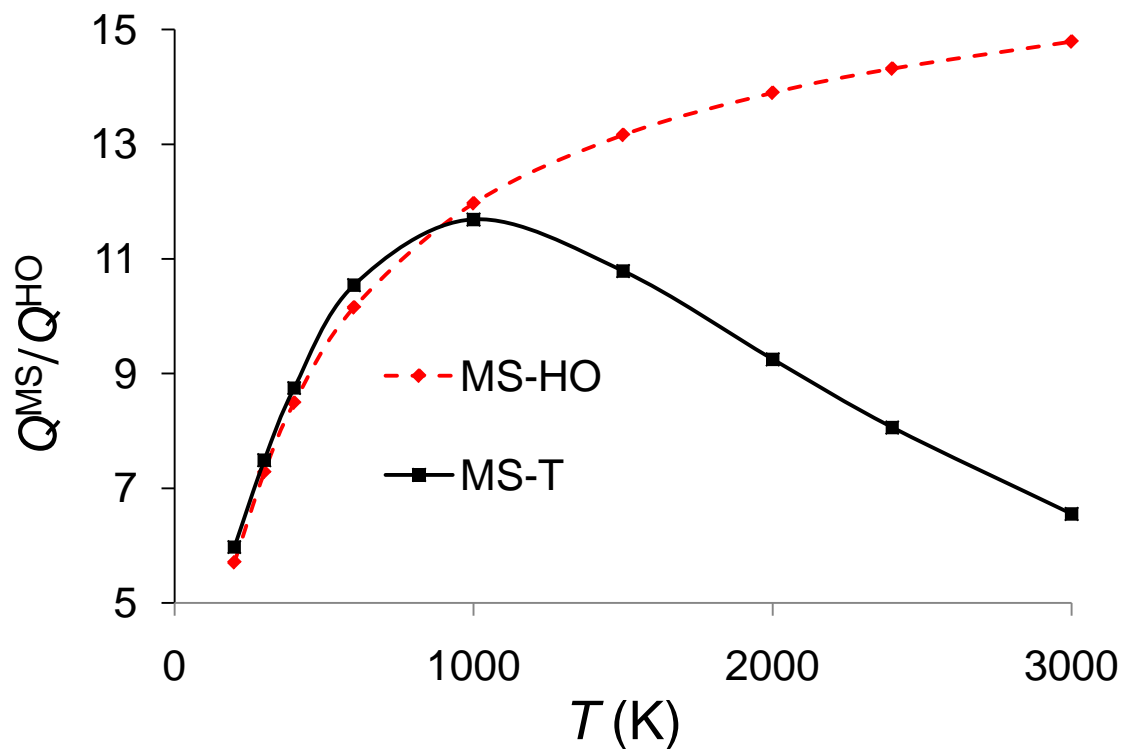
- We proposed a new approximation called the multi-structural method with torsional anharmonicity (MS-T) to calculate conformational-vibrational-rotational partition functions.
- It is applicable for molecules with multiple torsions coupled with overall rotation, each other, and/or with other low-frequency modes
- Assigning each torsion to a specific normal mode is not required.
- It has low computational cost, requiring no torsion barriers or scans.

# Effect of conformational entropy and torsional anharmonicity on the butanol partition function



Ratio of the conformational-rovibrational partition function of butanol calculated by the **multi-structural method** to that calculated by the single-structure HO approximation at the global minimum.

# 1-pentyl radical



Ratio of the conformational-rovibrational partition function of 1-pentyl radical calculated by the multi-structural method to that calculated by the single-structure HO approximation at the global minimum.

# Equations: Multi-structural torsion method

number of structures

**No barrier info, no scans.**

number of torsions

$$Q_{\text{con-rovib}}^{\text{MS-T}} = \sum_{j=1}^J Q_{\text{rot},j} \exp(-\beta U_j) Q_j^{\text{HO}} Z_j \prod_{\tau=1}^t f_{j,\tau}$$

$$f_{j,\tau} = \frac{\bar{\omega}_{j,\tau} \sqrt{2\pi\beta I_{j,\tau}}}{M_{j,\tau}} \exp(-\beta I_{j,\tau} \bar{\omega}_{j,\tau}^2 / M_{j,\tau}^2) I_0(\beta I_{j,\tau} \bar{\omega}_{j,\tau}^2 / M_{j,\tau}^2)$$

$$Z_j = \frac{g Q_{\text{rot},j} Q_j^{\text{HO}} + (1-g) Q_j^{\text{imp}}}{Q_{\text{rot},j} Q_j^{\text{HO}}} =$$

$$Q_j^{\text{imp}} = Q_{\text{rot},j} Q_j^{\text{HO}} Z_j^{\text{int}} Z_j^{\text{coup}}$$

$$g = \left( \prod_{\tau=1}^t \tanh \frac{q_{j,\tau}^{\text{FR}}}{P_{j,\tau} q_{j,\tau}^{\text{CHO}}} \right)^{1/t}$$

$$Z_j^{\text{int}} = \frac{\prod_{m=1}^{F-t} \bar{\omega}_{j,m}^{-1} \prod_{\tau=1}^t \bar{\omega}_{j,\tau}^{-1}}{\prod_{m=1}^F \omega_{j,m}^{-1}}$$

$$Z_j^{\text{coup}} = \left( \frac{|\det \mathbf{S}_j|}{|\det \mathbf{I}_j^{\text{rot}}| \prod_{\tau=1}^t I_{j,\tau}} \right)^{1/2}$$

For other slides in this presentation,  $Z_j$  is not included yet.

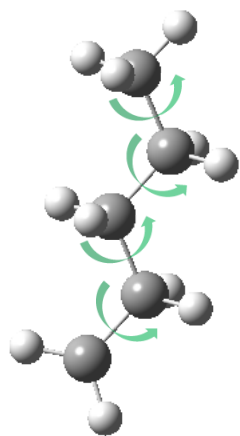
# The 1, 4-Hydrogen Shift Isomerization of the 1-Pentyl Radical

Multistructural anharmonicity is dominated by torsions in the potential energy surface of the reaction.

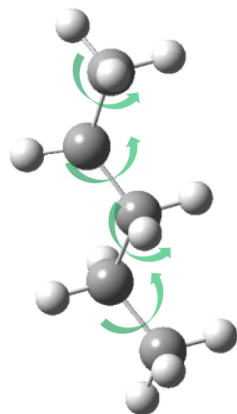
Reactant: 1-pentyl 4 torsions, 15 distinct structures

Product: 2-pentyl 4 torsions, 7 distinct structures

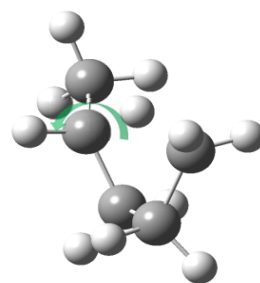
Transition state: 1 torsion, but 2 distinct structures (due to the ring inter-conversion)



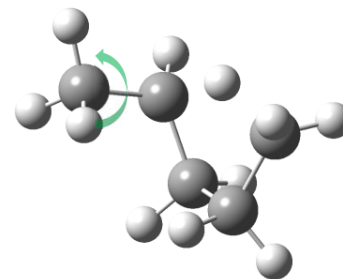
1-pentyl



2-pentyl



TS-1



TS-2

# A practical approach to compute the rate constant

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

**tunneling based on a single reaction path (ground-state transmission coefficient)**

**separable multi-structure anharmonicity factor**

---

## Reaction path for variational effects and tunneling

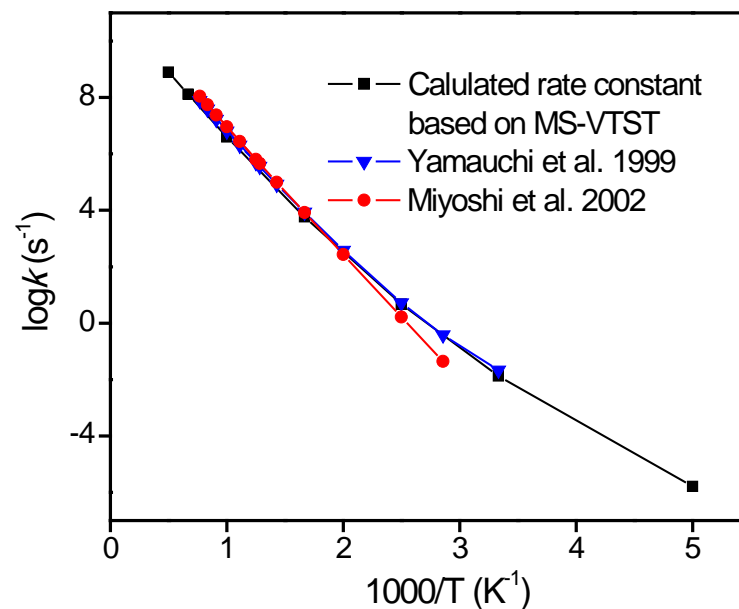
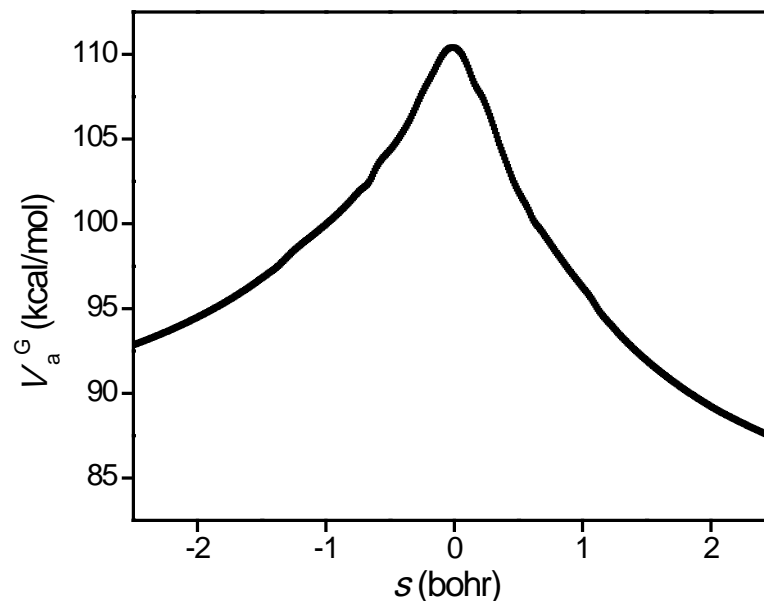
Multi-configuration Shepard Interpolation:

- PES of 1-pentyl and 2-pentyl by MM3 force field
- 9 Shepard-points (energy, gradient, Hessian) by M06 functional

# The 1, 4-Hydrogen Shift Isomerization of the 1-Pentyl Radical (cont.)

Multi-structure  
anharmonicity factors  $F^{\text{MS-T}}$   
for reactant, TS, and product

T (K)	$F^{\text{R}}$	$F^{\ddagger}$	$F^{\text{P}}$
300	6.8	2.0	11.0
600	10.0	2.2	14.1
1000	11.9	2.2	14.0
1500	12.9	2.0	11.9
2000	11.7	1.9	9.6

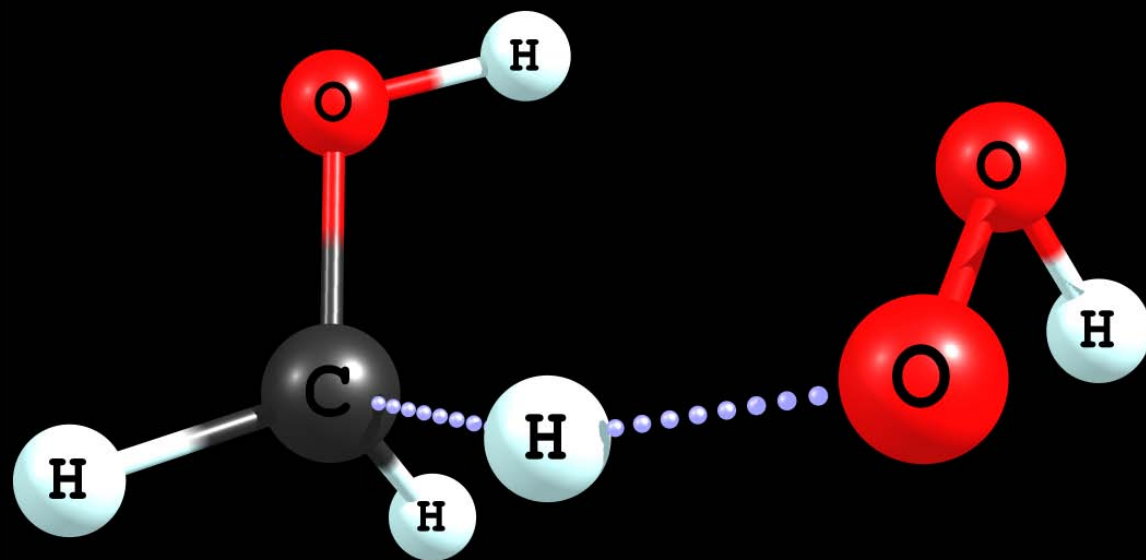


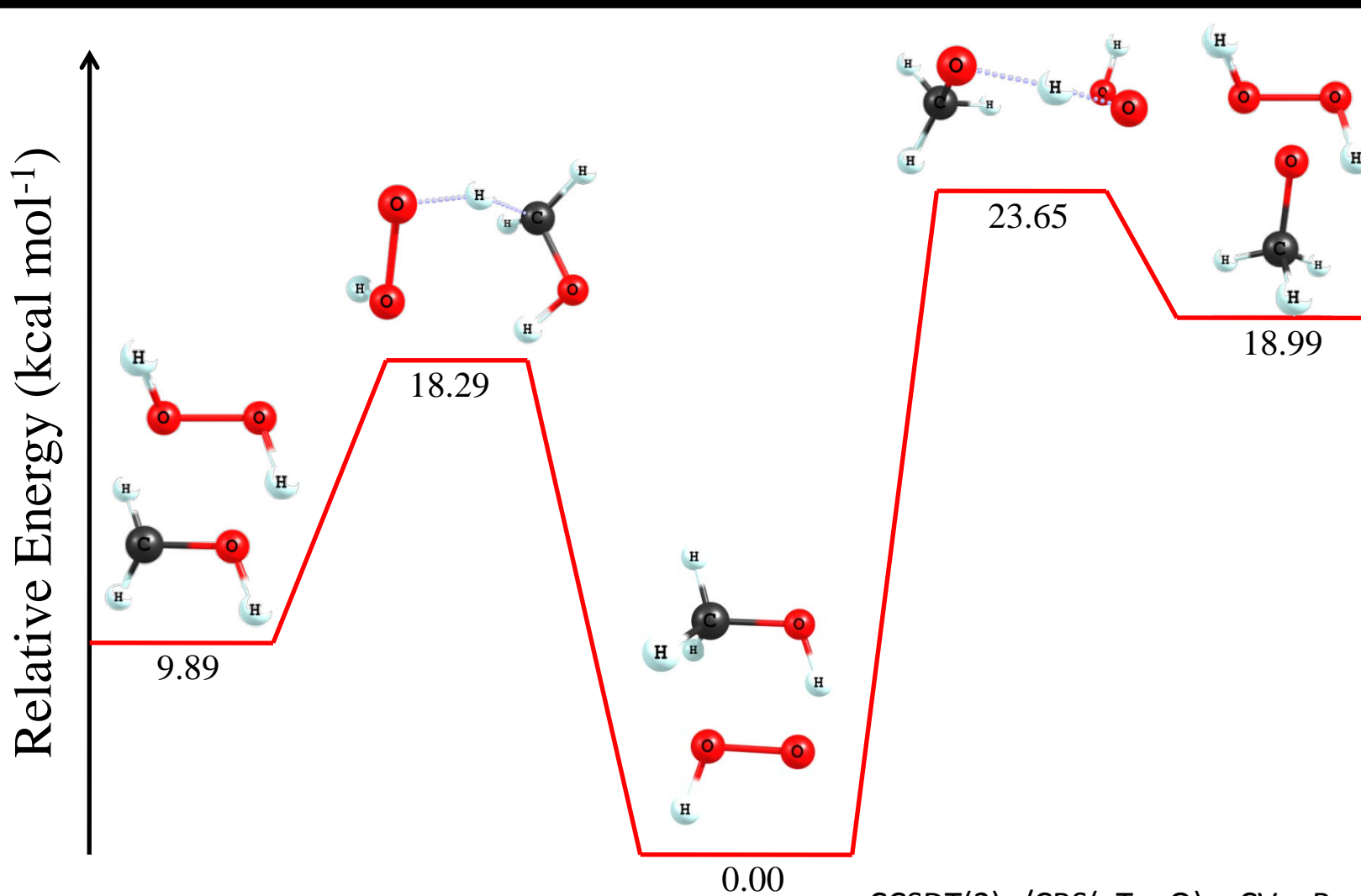
For this slide,  $Z_j$  is not included yet.

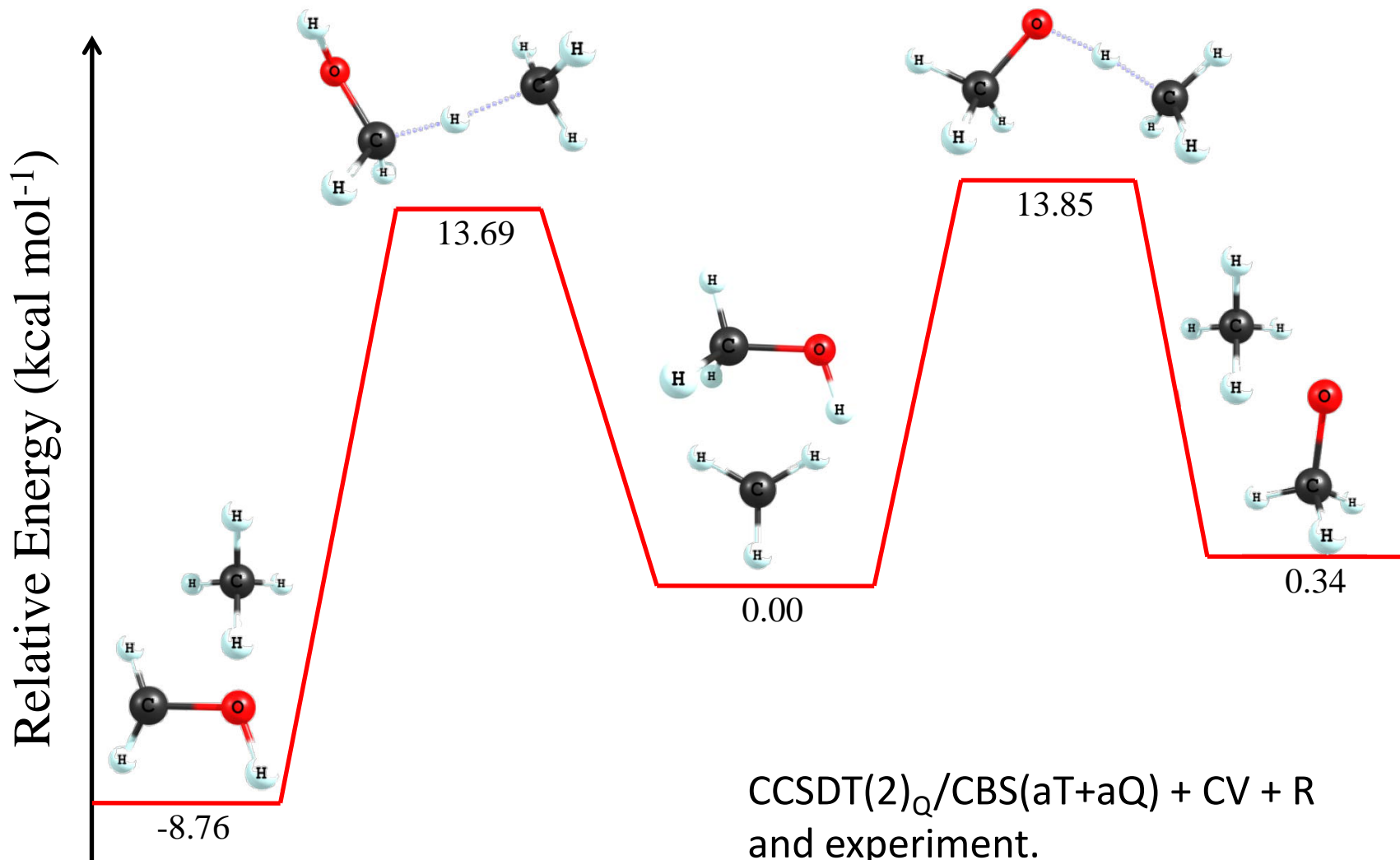


# John Alecu's poster

## ■ The Reactions:







# Accuracy vs. cost

Electronic Model Chemistry scaling	Mean Unsigned Error (MUE) (kcal mol <sup>-1</sup> )			
	$\Delta E$	$V^\ddagger$	Average	Cost
<b>N<sup>9</sup></b>				
CCSDT(2) <sub>Q</sub> /CBS(aT+aQ) + CV + R	0.3	0 (by def.)		78,000
<b>N<sup>8</sup></b>				
CCSDT/CBS(T+Q) + CV + R	0.1	0.2	0.1	16,000
<b>N<sup>7</sup></b>				
CCSD(T)-F12b/aug-cc-pVTZ	0.2	0.3	0.2	4,900
CCSD(T)/CBS(D+T)	0.2	0.5	0.4	900
<b>CBS-QB3</b>	<b>0.2</b>	<b>1.2</b>	<b>0.9</b>	<b>48</b>
MCG3-MPW	0.3	0.6	0.5	39
<b>N<sup>6</sup></b>				
BMC-CCSD	1.0	0.4	0.6	19
<b>N<sup>4</sup></b>				
M08-HX/maug-cc-pVTZ	0.5	0.8	0.7	43
M08-HX/ma-TZVP	1.0	0.8	0.8	25

- all calculations based on geometries optimized with M06-2X/MG3S
- single-processor CPU time relative to equivalent HF/cc-pVDZ calculation

# Fitting rate constants

## Conventional model

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

## New model

*proposed in J. Zheng and D. G. Truhlar, PCCP 12, 7782 (2010).*

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

This new form may be a much better way to fit curved Arrhenius plots than the almost universally used first form. This could have significant effects on combustion mechanisms and the representation of rate data in such

mechanisms