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.
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: \textbf{Multi-structural torsion method}

\textbf{No barrier info, no scans.}

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

\[ f_{j,\tau} = \frac{\sqrt{2\pi} I_{j,\tau}}{M_{j,\tau}} \exp\left(-\beta I_{j,\tau} \frac{\omega_{j,\tau}^2}{M_{j,\tau}^2}\right) I_0 \left(\beta I_{j,\tau} \frac{\omega_{j,\tau}^2}{M_{j,\tau}^2}\right) \]

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

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

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

\[ Z_j^{\text{coup}} = \left( \frac{\det S_j}{\det I_{j}^{\text{rot}} \prod_{\tau=1}^{t} I_{j,\tau}} \right)^{1/2} \]

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)
A practical approach to compute the rate constant based on a single reaction path (ground-state transmission coefficient)

\[ k = \kappa^G(T) \frac{\tilde{k}T}{h} \min_s \frac{Q^{GT,HO}(T,s)}{Q^{\ddagger,HO}(T)} \frac{Q^{\ddagger,MS-T}_{\text{con-rovib}}(T)}{Q^{R,MS-T}_{\text{con-rovib}}} \exp\left(-\frac{V(s)}{\tilde{k}T}\right) \]

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 $F^{MS-T}$ for reactant, TS, and product

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$F^R$</th>
<th>$F^\ddagger$</th>
<th>$F^P$</th>
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<tr>
<td>300</td>
<td>6.8</td>
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<td>1000</td>
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<td>1500</td>
<td>12.9</td>
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<td>2000</td>
<td>11.7</td>
<td>1.9</td>
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</table>

Calculated rate constant based on MS-VTST

Yamauchi et al. 1999
Miyoshi et al. 2002

For this slide, $Z_j$ is not included yet.
The Reactions:

- $\text{CH}_3\text{OH} + \text{HO}_2 \rightarrow \text{CH}_2\text{OH} + \text{HOOH}$ \hspace{1cm} (R1a)
- $\rightarrow \text{CH}_3\text{O} + \text{HOOH}$ \hspace{1cm} (R1b)

- $\text{CH}_3\text{OH} + \text{CH}_3 \rightarrow \text{CH}_2\text{OH} + \text{CH}_4$ \hspace{1cm} (R2a)
- $\rightarrow \text{CH}_3\text{O} + \text{CH}_4$ \hspace{1cm} (R2b)
Relative Energy (kcal mol$^{-1}$)

CH$_3$OH + HO$_2$

CCSDT(2)$_Q$/CBS(aT+aQ) + CV + R and experiment.
Relative Energy (kcal mol⁻¹)

-8.76

13.69

0.00

13.85

0.34

CCSDT(2)_Q/CBS(aT+aQ) + CV + R and experiment.

CH₃OH + CH₃
## Accuracy vs. Cost

<table>
<thead>
<tr>
<th>Electronic Model Chemistry</th>
<th>Mean Unsigned Error (MUE) (kcal mol⁻¹)</th>
<th>( \Delta E )</th>
<th>( V^* )</th>
<th>Average</th>
<th>Cost</th>
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<td>0 (by def.)</td>
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<tr>
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<td>0.6</td>
<td>19</td>
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<td>M08-HX/maug-cc-pVTZ</td>
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<td>0.5</td>
<td>0.8</td>
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<td>M08-HX/ma-TZVP</td>
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<td>0.8</td>
<td>25</td>
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</table>

- 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

\[ k = A \left( \frac{T}{300 \, K} \right)^n \exp\left( -\frac{E}{RT} \right) \]

New model


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

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.