

Multireference Correlated Wavefunction Calculations and Reaction Flux Analyses of Methyl Ester Combustion

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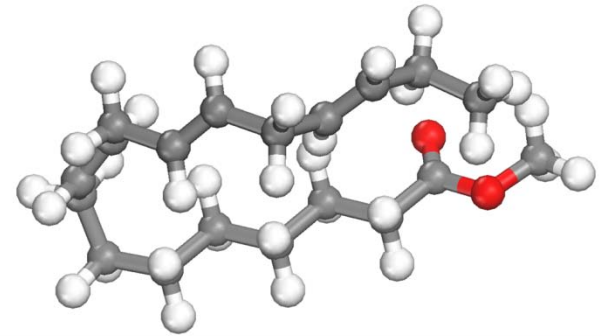
\$: NSF, A*STAR, DOE-BES

See Victor Oyeyemi's poster today

Biodiesel Molecule Combustion

Common biodiesel derived from rapeseed oil and soybeans:

- ❑ Methyl esters ($R(C=O)OCH_3$): methyl palmitate ($C_{17}H_{34}O_2$), stearate ($C_{19}H_{38}O_2$), oleate ($C_{19}H_{36}O_2$), linoleate ($C_{19}H_{34}O_2$), linolenate ($C_{19}H_{32}O_2$) – first two fully saturated, last three increasing number of C=C bonds
- ❑ Predict pyrolysis reaction energetics: breaking C-H, C-C, C=C, C-O, C=O bonds
- ❑ Predict kinetics of most important/most uncertain combustion reaction steps
- ❑ Compare to smaller methyl esters to test “group additivity”
- ❑ How to treat such large molecules with accurate QM? MRSDCI $O(N^6)$... fast new algorithms for accurate QM.



Thermochemical Kinetics from Quantum Chemistry

❑ Structure Optimization

- Conformation Search for Global and Statistically Favored Minima using Molecular Mechanics (Classical Force Fields)
- Local Refinement at Hartree-Fock and/or DFT B3LYP Levels

❑ Thermochemistry

- C-H, C-C, C-O bond dissociation energies using CASSCF/L-MRSDCI/L-MRAPCF with basis set extrapolation

❑ Kinetics

- Reaction Flux and Sensitivity Analyses to identify most important/most uncertain reaction steps
- DFT B3LYP determination of reaction paths/structures and zero point energies/thermal corrections
- L-MRSDCI /MRACPF prediction of activation energies

Multireference Configuration Interaction (MRCI)

Configuration Interaction Expansion

$$\Psi^{CI} = \sum_R c_R \Psi_R + \sum_{i,a} c_i^a \Psi_i^a + \sum_{ij,ab} c_{ij}^{ab} \Psi_{ij}^{ab} + \sum_{ijk,abc} c_{ijk}^{abc} \Psi_{ijk}^{abc}$$

$\xrightarrow{\text{(MR)CIS}}$
 $\xrightarrow{\text{(MR)CISD}}$

Solve eigenvalue equation : $\mathbf{HC} = \mathbf{EC}$

$$\begin{bmatrix} \langle \Psi_0 | H | \Psi_0 \rangle & \langle \Psi_0 | H | \Psi_i^a \rangle & \dots & \langle \Psi_0 | H | \Psi_{ij}^{ab} \rangle \\ \langle \Psi_i^a | H | \Psi_0 \rangle & \langle \Psi_i^a | H | \Psi_i^a \rangle & \dots & \langle \Psi_i^a | H | \Psi_{ij}^{ab} \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \Psi_{ij}^{ab} | H | \Psi_0 \rangle & \langle \Psi_{ij}^{ab} | H | \Psi_i^a \rangle & \dots & \langle \Psi_{ij}^{ab} | H | \Psi_{ij}^{ab} \rangle \end{bmatrix} \begin{bmatrix} c_0 \\ c_i^a \\ \vdots \\ c_{ij}^{ab} \end{bmatrix} = E \begin{bmatrix} c_0 \\ c_i^a \\ \vdots \\ c_{ij}^{ab} \end{bmatrix}$$

- Very large eigenvalue problem
- Only first few roots
- Direct diagonalization not practical => iterative methods

↓

$$(ia | jb) = \iint dr_1 dr_2 \phi_i(1) \phi_a(1) (1/r_{12}) \phi_j(2) \phi_b(2)$$

Davidson diagonalization
(E. R. Davidson, 1975)

$$\delta C_I = \frac{EC_I - Z_I}{H_{II} - E}$$

Constructing sigma vector, $Z_i = H_{ij} C_j$, is a major bottleneck.

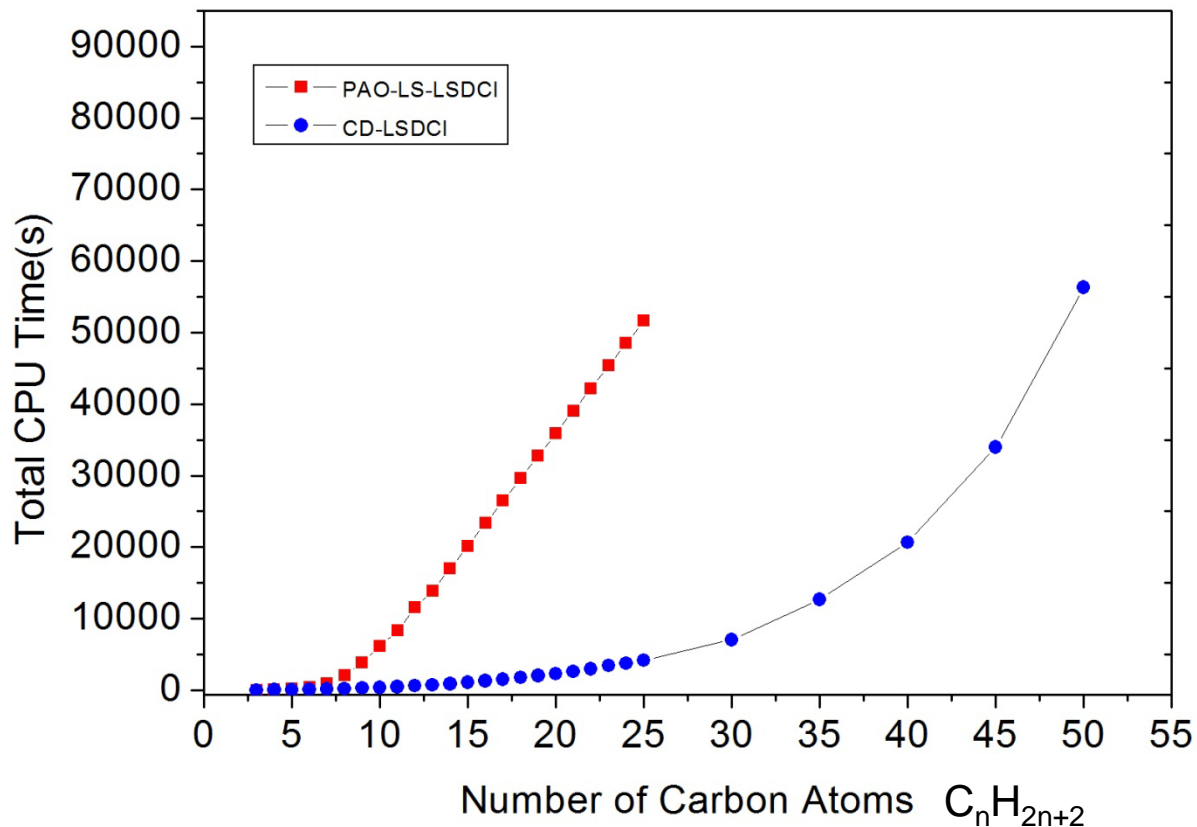
$$Z_{ac}^\lambda = \sum_{\mu,b,d} (ab | cd) C_{bd}^\mu$$

Conventional scaling of electronic structure methods

Method	Scaling	Method	Scaling
HF	O(N ⁴)	CCSD	O(N ⁶)
KS-DFT	O(N ³)	CCSD(T)	O(N ⁷)
MP2	O(N ⁵)	MRSDCI	O(N ⁶)
MP4	O(N ⁷)	FCI	O(N!)

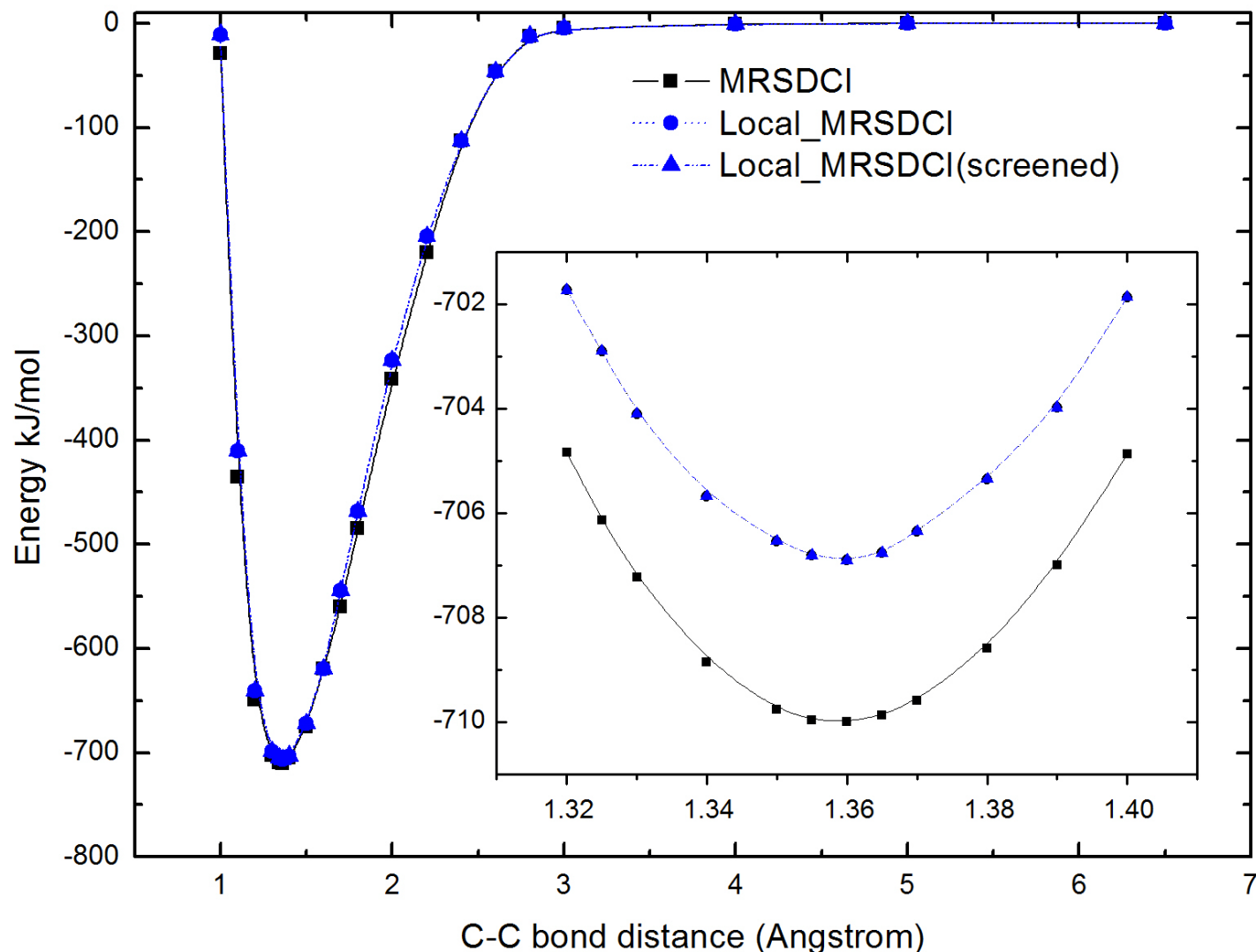
PAO LS-LSDCI versus CD-LSDCI: Timings

Total CPU Time for PAO based LS-LSDCI and CD-LSDCI



Linear scaling of 2008 PAO/IS algorithm lost (CD is $O(N^{2-3})$ scaling) but prefactor much lower
⇒ larger molecules (~50 heavy atoms) accessible w/no loss of accuracy (μ Hartree error)
However, CI is not size-extensive => error grows with system size...

L-MRSDCI-IS BREAKS BONDS SMOOTHLY AND ACCURATELY: SCREENING RETAINS μH ACCURACY; LMRSDCI RECOVERS >98% CORR.



PES along the reaction coordinate for bond cleavage along the C=C bond in trans-6-dodecene ($\text{C}_{12}\text{H}_{24}$). Inset shows an expanded view of the curves.

Basis Set Extrapolation

- **Dunning-type basis sets:** correlation -consistent basis sets designed for extrapolation to the complete basis set (CBS) limit
 - cc-pVXZ where X=D, T, Q, 5, 6, for a sequence of added angular momentum functions
 - Computational cost limits the maximum cardinal number (X)

- **A Dual-Cardinal Extrapolation Scheme:**

- CASSCF energies and correlation energies are separately extrapolated

$$E^{tot} = E^{CASSCF} + E^{cor}$$

- A power law scheme proposed by Truhlar

$$E_X^{CASSCF} = E_{\infty}^{CASSCF} + A^{CASSCF} X_{\infty}^{-\alpha} \quad \alpha = 3.4^*$$

$$E_X^{cor} = E_{\infty}^{cor} + A^{cor} X_{\infty}^{-\beta} \quad \beta = 2.4^{**}$$

* Optimized for HF

** Optimized for CCSD

Halkier, A et al. , *Chemical Physics Letters* **1998**, 286 (3-4), 243-252.

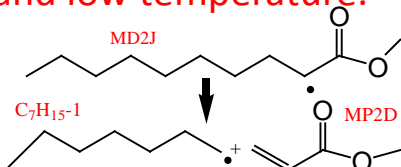
Truhlar, D. G., *Chemical Physics Letters* **1998**, 294 (1-3), 45-48.

Reaction Flux and Sensitivity Analyses

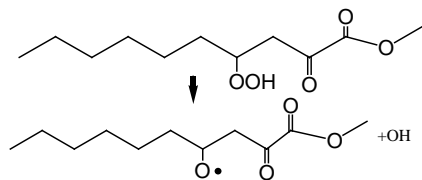
Consider largest surrogate for biodiesel for which combustion mechanism available.
Reduced methyl decanoate mechanism used as input to Chemkin-Pro ...
(Help from Ju and Green groups greatly appreciated!)

➤ Reaction flux analysis of reduced combustion mechanism* for methyl decanoate at both low and high temperature to find main pathways.

• **β-scission reactions important at both high and low temperature.**



• Addition of O₂ produces a more complex mechanism at low temperature. Isomerization and decomposition of these species need more accurate data.

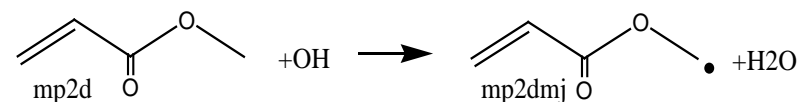


➤ Sensitivity analysis performed to determine the sensitive reactions under adiabatic conditions at 650-1200 K.

• Reactions of large molecule/radicals such as MD at low temperature are more sensitive than at high temperature.

• **Hydrogen abstraction reactions from large molecules sensitive at all temperatures.**

• A-factor sensitivity for concentrations of species is found to be small in general.



Connection to other C-EFRC Team Members and Expected Impact

□ Theory connections:

- Don Truhlar – calculation of VTST rate constants using LMRSDCI barriers/energetics as input
- Steve Klippenstein/Jim Miller – input for high pressure kinetics
- Bill Green – building/refinement of overall kinetic models
- ASCR collaboration with Mark Gordon to parallelize LMRSDCI code

□ Experimental connections:

- Fred Dryer – flow reactor studies
- Fokion Egolfopoulos – counterflow flame studies
- Yiguang Ju – jet stirred reactor/PIV/LIF/molecular beam MS

□ Expected Impact:

- Understanding of biodiesel molecule combustion reactions as a function of temperature and pressure.