Accurate \textit{ab initio} potential energy surface, dynamics, and thermochemistry of the \( \text{F} + \text{CH}_4 \rightarrow \text{HF} + \text{CH}_3 \) reaction

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Introduction

**Quasiclassical trajectory (QCT) calculations**

- **Nuclear motion: Classical mechanics**
  QCT requires around $10^7$–$10^8$ forces, *i.e.* potential gradients

- **Electronic motion: Quantum mechanics $\Rightarrow$ potential energies and gradients**

- **Direct dynamics**
  "on the fly" electronic energy and gradient computations
  expensive $\Rightarrow$ low level of theory

- **Semiempirical reaction specific Hamiltonians**

- **Analytical potential energy surfaces (PES)**
  differentiation of the PES $\Rightarrow$ inexpensive gradients
  *ab initio*-based *(higher level of theory)* or (semi)empirical

**Applications for the F + CH$_4$ $\rightarrow$ HF + CH$_3$ reaction**
Permutationally invariant potential energy surfaces in high dimensionality

**Permutational symmetry:** numerical efficiency (less coefficients) important for dynamics (e.g. isomerization)

\[
V = \sum_{m=0}^{M} C_m [y_{12}^a y_{13}^b y_{14}^c y_{23}^d y_{24}^e y_{34}^f]
\]

\[
m = a + b + c + d + e + f
\]

Morse variable

\[
y_{ij} = \exp(-r_{ij} / a)
\]

Linear least-squares fit to *ab initio* energies ⇒ \(D_m\) coefficients

**Implementation is based on the invariant polynomial theory**

\[
V(y) = \sum_{\alpha=1}^{M} \text{poly}_\alpha(p(y))q_\alpha(y)
\]

\(p(y): N(N-1)/2\) primary invariant polynomials

\(q_\alpha(y): \) secondary invariant polynomials

**Example: \(A_2B\)**

\[
p_1 = r_{12} \quad q_1 = 1
\]

\[
p_2 = (r_{13} + r_{23}) / 2
\]

\[
p_3 = (r_{13}^2 + r_{23}^2) / 2
\]
## Number of terms vs. total polynomial order

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Full-dimensional potential energy surface for the F + CH₄ reaction

**Ab initio data**

\[ E_{\text{PES}} = E_{\text{UCCSD(T)/aVDZ}} + E_{\text{UMP2/aVTZ}} - E_{\text{UMP2/aVDZ}} \]

Test of the composite approach
Reference: explicit UCCSD(T)/aug-cc-pVTZ
rms error (cm⁻¹)

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<th>Energy Component</th>
<th>Value</th>
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<td>( E_{\text{UMP2/aVDZ}} )</td>
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<td>( E_{\text{PES}} )</td>
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Data points
Complex region: FCH₄ 12384
Fragment channels:
- F + CH₄ 2000
- HF + CH₃ 2000
- H₂ + CH₂F 2000
- H + CH₃F 1000

**Fit to the ab initio data**

4! = 24 permutations of 15 \( r_{ij} \) for FCH₄

Without permutational symmetry: 54 264 terms
Using permutational symmetry: 3 250 terms

Fit
Number of free coefficients: 3250 + 12 (short-term repulsion)
RMS fitting errors
- 0–11000 cm⁻¹: 125 cm⁻¹
- 11000–22000 cm⁻¹: 222 cm⁻¹
- 22000–55000 cm⁻¹: 536 cm⁻¹

The $\text{F} + \text{CH}_4 \rightarrow \text{HF} + \text{CH}_3$ reaction

HF vibrational and rotational distributions

**QCT calculations**

\[ E_{\text{coll}} = 1.8 \text{ kcal/mol} \]

75 000 trajectories


Correlated HF/DF and umbrella excited CD$_3$/CHD$_2$ vibrational populations at collision energy of 2.8 kcal/mol

F + CHD$_3$(v=0) → HF(v) + CD$_3$(0v$_2$00)

F + CHD$_3$(v$_1$=1) → HF(v) + CD$_3$(0v$_2$00)

F + CHD$_3$(v=0) → DF(v) + CHD$_2$(000v$_4$00)

F + CHD$_3$(v$_1$=1) → DF(v) + CHD$_2$(100v$_4$00)
Conclusions

“In order to find a similar quality of calculations for a global PES, one would need to compare the present result with those carried out for three atom systems. This work thus represents a major breakthrough in the determination of a global PES for a polyatomic system.”

“This study also shows that an approach as QCT is capable to explain many experimental features in a polyatomic reaction as long as an accurate PES is used.”

Referee report for