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# Opportunities for Computational Chemical Kinetics in Combustion

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# Chemical Kinetics: *Outline*

**Outline:**

- **Conquering the Tyranny of Dimensions**
- **Quantum Dynamical Rates for All**
- **Founding Energy Transfer on First Principles**

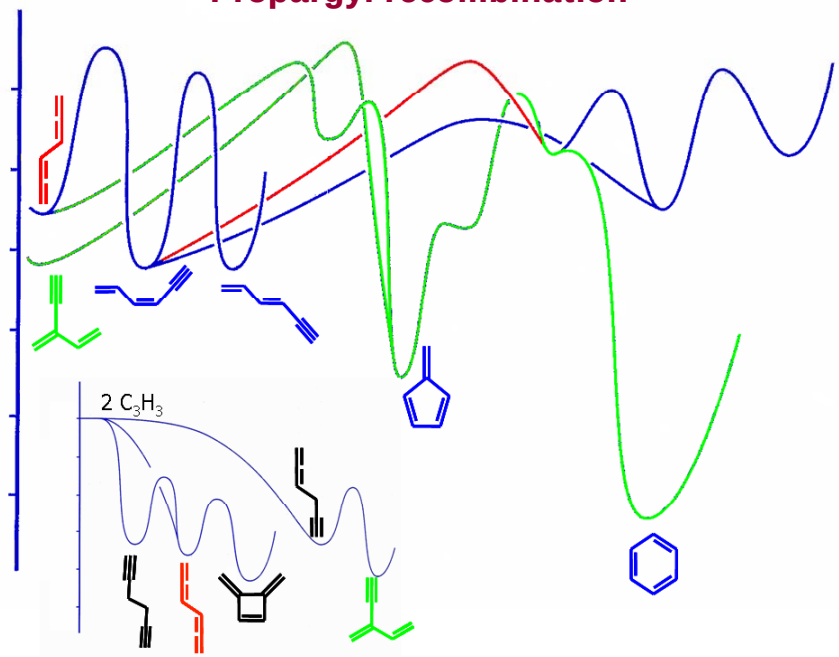
## Chemical Kinetics: *Tyranny of Dimensions*

**Problem**

- **3n-6 internal coordinates for n n atoms in a reaction**
  **=> benzene has 30 degrees of freedom**

- **complete combustion breaks every bond in a hydrocarbon**
  **=> numbers of radicals accessible and important can grow exponentially with the number of degrees of freedom**

**Propargyl recombination**



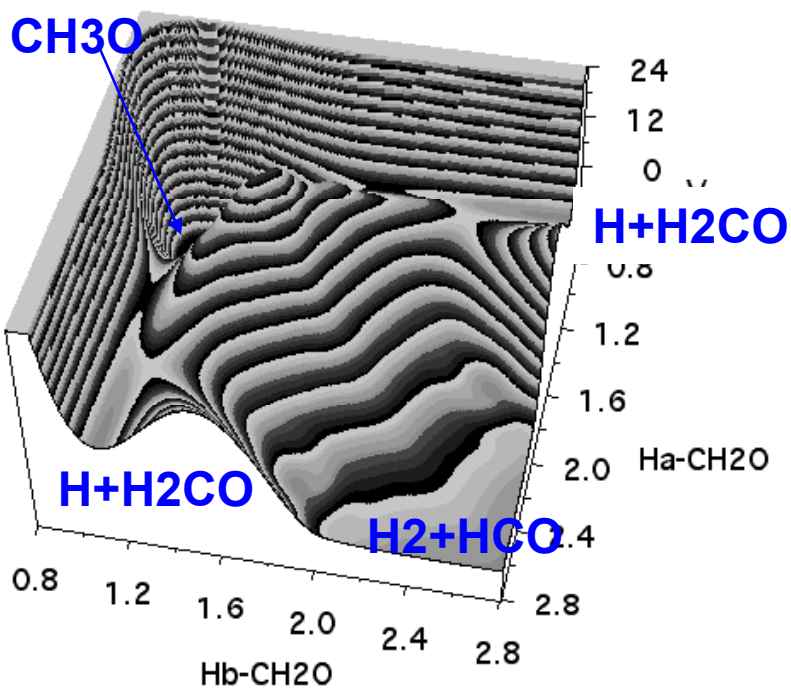

**=>Current computational limitations are**

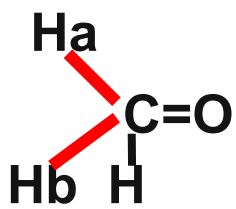
- ***not* in characterization cost of any one reaction pathway for reactants**
- **in "manual" discovery and characterization of all important reaction pathways for reactants**

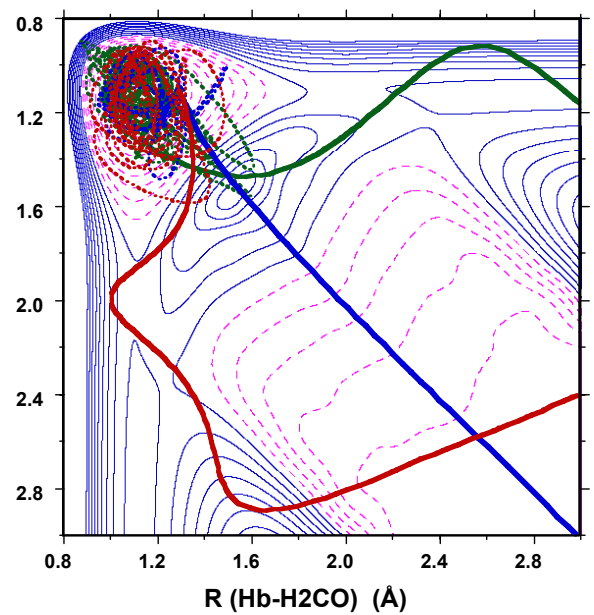
## Chemical Kinetics: *Tyranny of Dimensions*

- **Discovery of important reaction pathways can go beyond saddle points and steepest descent reaction paths**

- **For example, in CH3O dissociation, ~15% of products (H2+HCO) follow a reaction pathway that does not have a saddle point**



## On Going Research:

### 1. Kinetics-Driven Potential Energy Surface (PES) Generation

- **non-systematic application with trajectories or transition state theory**
  **- often lower quality, cheap electronic structure methods**
  **- often no generation of PES fit**
  **(how CH3O -> H2+HCO was discovered)**

- **developing black-box PES fitting methods that have local fitting error measures (Collins, Thompson)**
  **- generate PES fit with on-the-fly PES calculations**
  **- call for electronic structure calculation only if local fitting error requires it**
  **- need only energies but can use gradients and hessians**

**On Going Research:**

## 2. Automated Combustion Kinetics

- **Klippenstein and Harding are teaching computers:**

  **- "rules" for searching for PES saddle points and transition states**

  **- interactive kinetics/quantum-chemistry methods to determine rates to accuracy needed (i.e., kinetics-driven PES generation)**

  **- to integrate above with semi-empirical energy transfer models (for pressure effects) into RRKM theory + Master Equation to produce rates and branching ratios as a function of T and P for a given set of reactants *with little human assistance***

**What the future holds:**

## Automated Combustion Kinetics

**Focus:**
- **demonstration on several well known complex reaction(e.g., C3H3+C3H3)**
- **systematic application**
  - **=> consistent thermal kinetics for a reaction family**
  - **=> human thinking focused on key particulars for each reactant pair**
  - **=> continual relearning of "rules" for kinetically important PES features**
  - **=> evolving library of PES fits for future reuse**

**Results: 2 years:** **successful demonstration**

**3-5 years:**
- **production application to systematic reviews of complex reaction families (e.g., aromatic radical chemistry)**
- **library of partial PESs for family of reactions**

**Resources:** **not likely intensive until into production**

**production dominated by electronic structure costs per PES feature**

- **both costs and number of features scale strongly with number of degrees of freedom**

## Problem

- **quantum effects in rate constants**
  **- selectively important in tunneling and non-adiabatic effects**
  **- very computer intensive (most applications stop at 4 atom systems)**

- **quantum effects are condensed into**
  **$P^J(E)$ = Cumulative Reaction Probability**

  $$k(T) = \Sigma_J (2J+1) \int_o P^J(E)\, e^{-E/kT}\, dE \,/\, hQ(T)$$

- **$P^J(E)$ in effect is a sum over contributions from each degree of freedom**
  **$P^J(E)$ can be adiabatically approximated for each degree of freedom (TST)**

- **Quantum effects tend to be local to the bonds being broken and formed**
  **=> only a few degrees of freedom likely to be quantum mechanical**
  **=> cost of calculating quantum effects ultimately *stops* growing with reactant sizes**

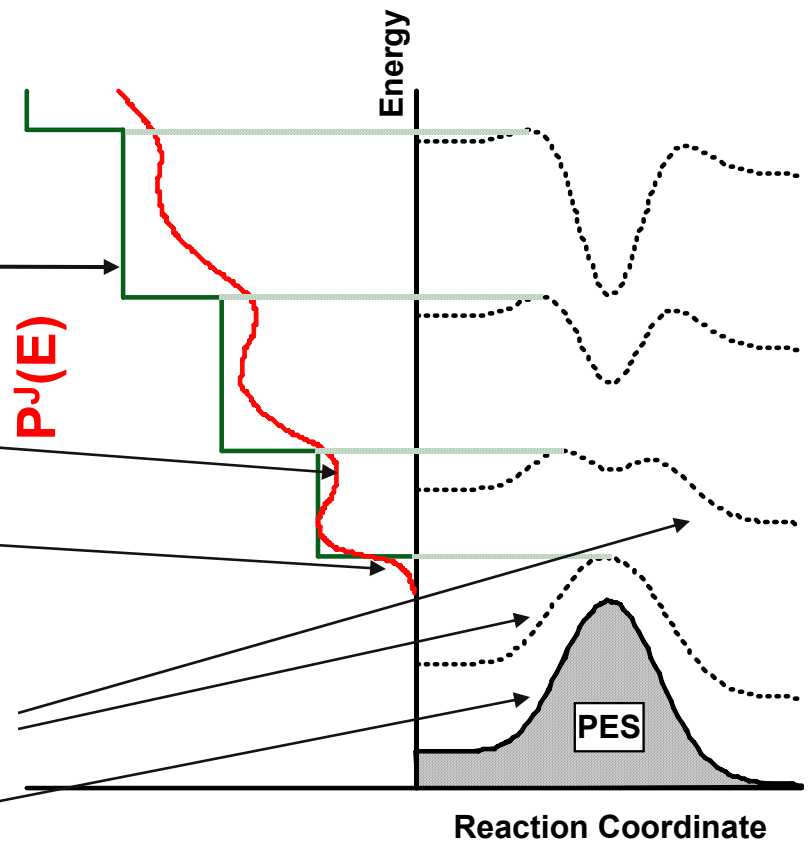
## Chemical Kinetics: *Quantum Dynamical Rates*

**Transition State Theory (TST)**

**=> no recrossing of adiabatic barrier**

**=> steps in $P^J(E)$**

- **Exact $P^J(E)$ has recrossing and tunneling**
- **Energy adiabatically locked in quantized vibrations away from rxn path**
- **Value of PES along rxn path**

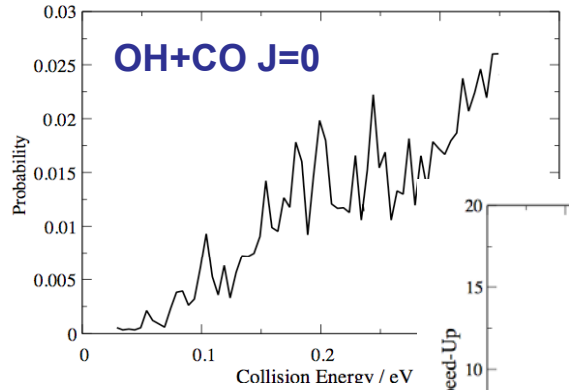


## On going Research:

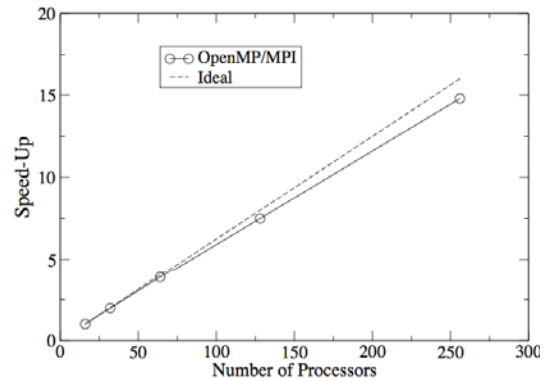
- **Time-dependent and Time Independent parallelized methods for $P^J(E)$**

**Time-dependent approach**

**$P^J(E)$ found by applying a flux operator to propagating wavepackets**

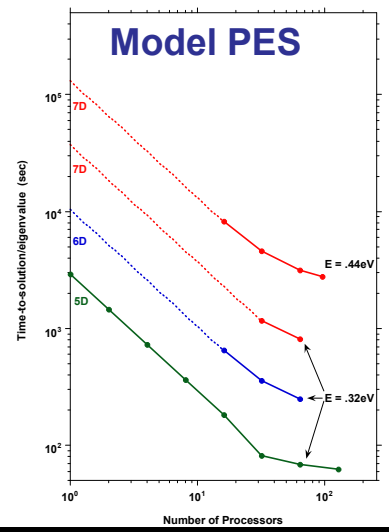



**S. K. Gray et al.**




**Time-independent approach**

**$P^J(E)$ found from iterative eigensolve of an operator involving two green's function**




**Minkoff and Wagner**

**What could the future hold:**

## Hybrid TST/Quantum-Dynamics determination of $P^J(E)$

**Focus:**
- **demonstrate that at transition state contributions to $P^J(E)$ can be treated**
  - **adiabatically for "remote" degrees of freedom**
  - **quantum calculated for "active" degrees of freedom**
  
  **on a family of direct reactions (e.g., O + alkanes)**
- **apply to selected direct and addition-elimination reactions**
- **develop "corrections" for TST to include in automated kinetics**

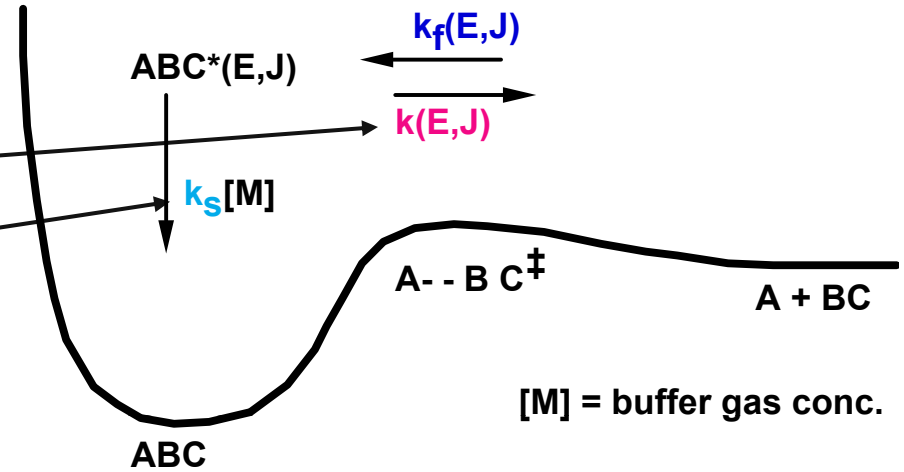
**Results: 2 years: successful demonstration**
**3 years: production applications to any reaction we have relevant PES for**

**Resources:**
- **maximum of ≤ 8 "active" degrees of freedom?**
- **problem scales ≥ cube of grid/basis dimension**

  **now 6 degrees of freedom problem => ~$10^2$ processors**
  **if ~10 basis functions per degree of freedom,**
  **biggest problems > $10^6$ processors**

## Problem

**To include pressure effects,**
**competition between:**
**- unimolecular decay k(E,J)**
**- collisional energy transfer $k_s$**




**=> master equation formulation**
**=> energy transfer probabilities**
**=> energy transfer moments**
**e.g., $\Delta E_{down}$ = average energy loss**
**=> now energy transfer is adjustable parameter**
**- rules of thumb for its value**
**- little sensitivity to effects of isomers, polar forces, etc.**
**- little sensitivity to inelastic resonances, super inelastic collisions**

## On Going Research:

### Classical Trajectory studies of relevant energy transfer

- **Some calculations of energy transfer out of highly energetic species**
  **- almost always molecules + atom**
  **- simple PES weakly uniformed by accurate electronic structure calc.**

- **A few pioneering calculations (Miller, Schatz) of energy transfer**
  **- out of highly energetic small radicals**
  **- ab initio PES**

**What could the future hold:**

## Automated Generation of Energy Transfer Rates

**Focus:** • demonstrate automated energy transfer rates for master equations
- generate energy transfer moments via trajectories on PESs fit with on-the-fly PES calculations
- call for electronic structure calculation only if local fitting error requires it
- converge calculation to the few lowest moments of the energy transfer which control probabilities

on family of simple recombination reactions (e.g., alkyl radical + Ar)

• apply as part of automated kinetics

**Results:** 2 years: successful demonstration
3 years: incorporation into automated kinetics

**Resources:** dominated by electronic structure costs and number of isomers
- both increase with degrees of freedom
- relatively cheap electronic structure methods may work
- isomer dependence may be modest

# Chemical Kinetics: *Summary*

**Outline:**

- **Tyranny of Dimensions**

**Automated Combustion Kinetics**

- **Quantum Dynamical Rates for All**

**Hybrid TST/Quantum-Dynamics determination of $P^J(E)$**

- **Founding energy transfer on first principles**

**Automated Generation of Energy Transfer Rates**