Reactions involving the formation and transformation of H_3^+

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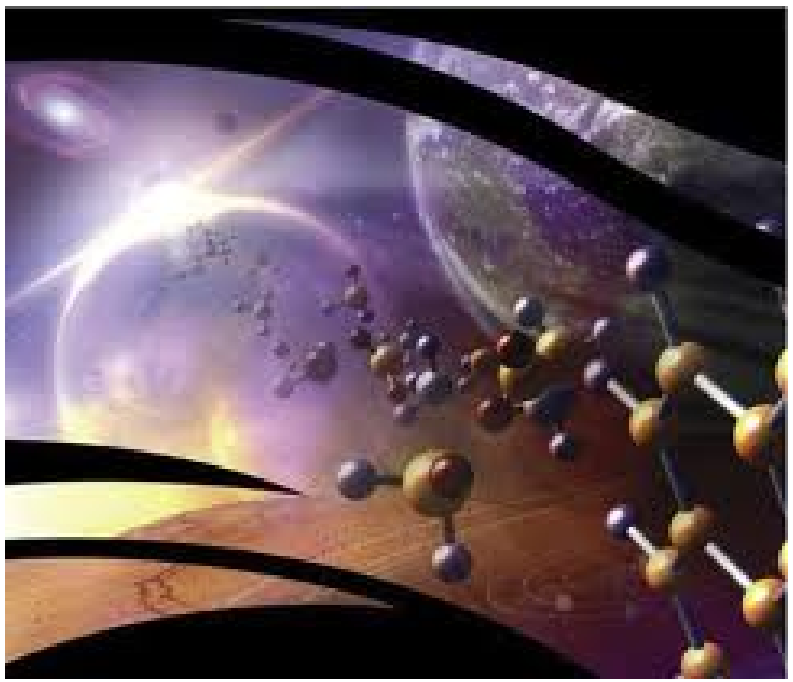
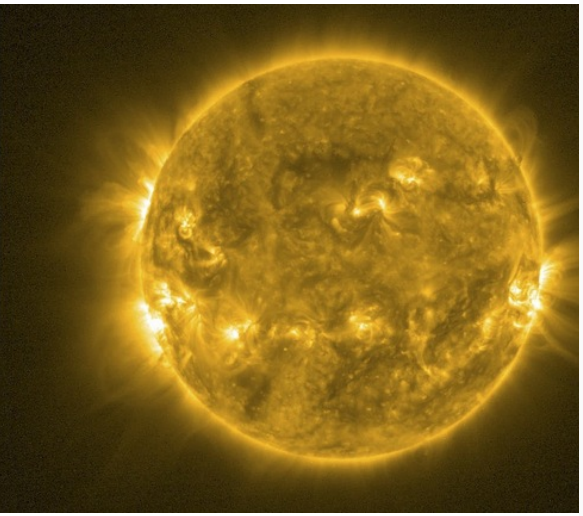


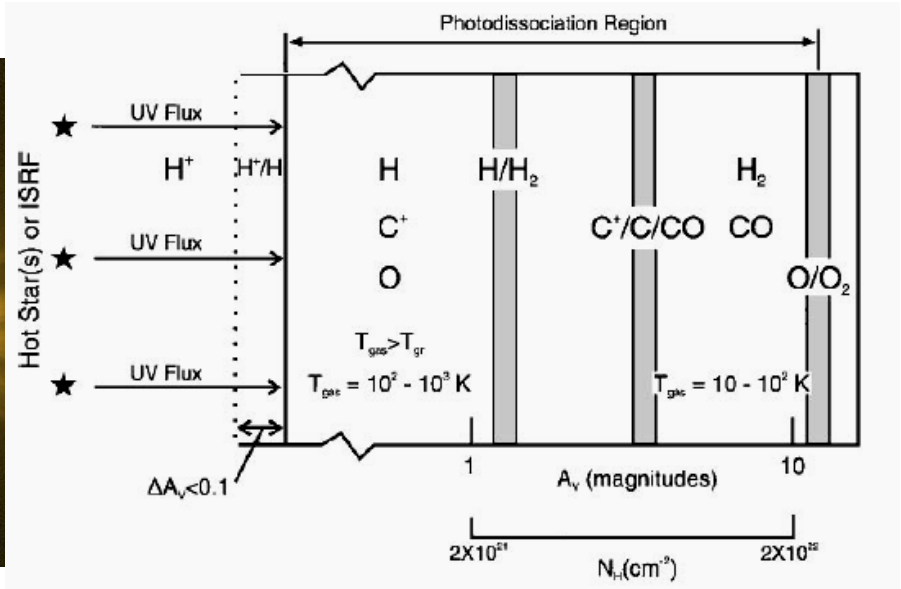
Outline

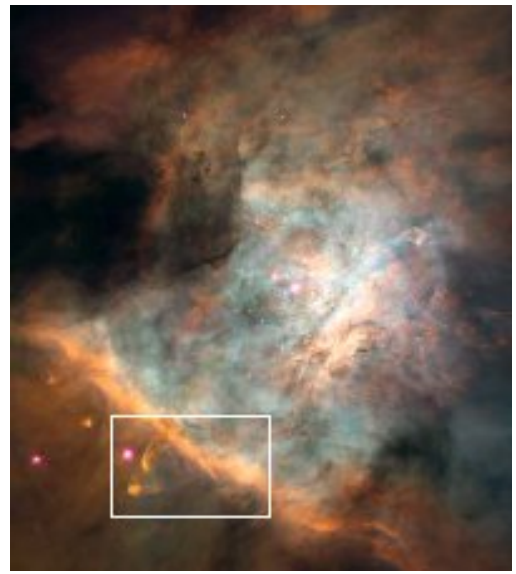
1. Introduction
2. H_n^+ PES's
3. H_2+H_3^+ exchange reaction
4. H_2+H_2^+ direct reaction
5. Conclusions

Molecular Universe



Hollenbach & Tielens, Annu. Rev. Astrophys. ('97)





Stellar atmosphere:
atomic lines
Atom+Atom collisions
Magnetic fields
Polarization of lines
Hanle effect

PDR
Formation of H_2
act as shield for other molecules
$M^+ + H_2 \rightarrow MH^+ + H$
$M + H_3^+ \rightarrow MH^+ + H_2$

Molecular clouds
low temperatures
varying densities
formation of complex molecules

Chemical pumping in molecular clouds and PDR's

- Exothermic reactions of H_2 with atoms and ions

$$H_2(v=0) + O^+ \rightarrow OH^+(v', j') + H$$ Gómez-Carrasco, *et al.* ApJ,('14)

- Chemistry of $H_2(v > 0)$ in ISM Agúndez, *et al.* ApJ, **713**,662 ('10)

Initial state dependent chemistry

$$H_2(v=1) + C^+ \rightarrow CH^+(v', j') + H$$ Zanchet, *et al.* ApJ,**766**,80 ('13)

$$H_2(v>1) + S^+ \rightarrow SH^+(v', j') + H$$ Zanchet, *et al.* AJ,**146**,125 ('13)

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- The most abundant ion is H_3^+
  - H_2^+ disappears rapidly in the exothermic $H_2 + H_2^+ \rightarrow H_3^+ + H$ reaction
  - However $H_2 + H_3^+ \rightarrow H_3^+ + H_2$ (ortho/para conversion, deuteration)
  - H_3^+ is very reactive with other species:

$$H_3^+ + O \rightarrow H_2 + OH^+$$
$$H_3^+ + O_2 \rightarrow H_2 + O_2H^+$$

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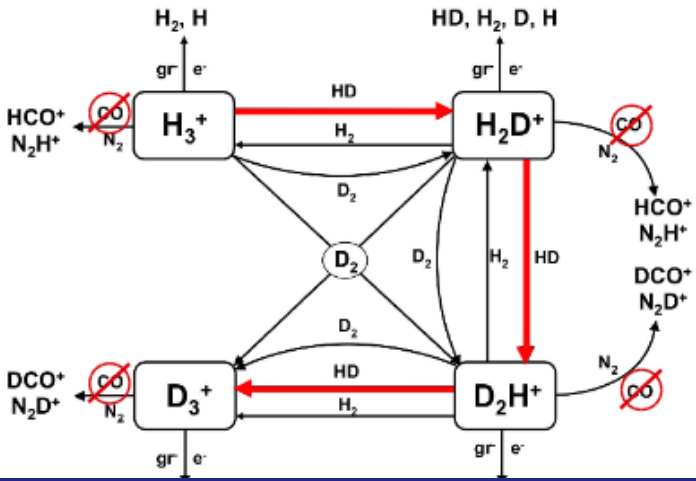

- at low T molecules freeze

- H_3^+ "lives" longer time

- H_3 Deuteration occurs

- Key process for high D/H

Previous studies on H_4^+.

- Experimental

  H_2+$H_2^+(v = 0 - 3) \rightarrow H_3^+$ + H and isotopic variants

  Koyano & Tanaka ('80) ; Anderson *et al.* ('81) , Krenos *et al.*('76) , ...

  H_3^+ infrared spectra, produced in the previus reaction

  Carrington & Kennedy ('84); ...

- Simulation of the potential

  Diatomics-in-Molecules potential Muckerman *et al.* ('81)

  PES with frozen H_3^+ Alvarez-Collado *et al.* ('94)

  Interpolated PES in the H+H_3^+ channel Moyano *et al.* ('04)

  Stationary points and intersections along the MEP Varandas ('08)

  No accurate global PES available

- $H_2^+ + H_2 \rightarrow H_3^+ + H$ collision simulations

  Quasi-Classical trajectories, with Surface hopping using DIM

  Stine & Muckerman (1976,...) ; Tully & coworkers (1976,...) ; Schatz & coworkers (1985,...) ; ...

$H_2 + H_3^+$ exchange collision: ortho/para conversion

- QCT calculations: Moyano & Collins, ('03)
- 7D Quantum WP with reduced dimensions: Bowman & co. ('10)
- Statistical approaches including spin statistics:

  Park & Light (2007) Hugo *et al.* (2009) McCall *et al.* (2011)

Objectives

- Full dimensional PES for H_4^+ and H_5^+

  with good long range behavior
  with analytical derivatives and non-adiabatic couplings

- H_2+ $H_3^+ \rightarrow H_3^+$+H_2 Is the reaction statistical?:

  Going beyond pure statistical approach Parker& Light('07), Hugo *et al.*('09)
  - Introduction of dynamical bias
  - Use global PES

  Comparison with experimental $K^{hop}/K^{exchange}$ McNab and coworkers ('11)

- H_2+ $H_2^+ \rightarrow H_3^+$+H

  Non adiabatic couplings and Conical intersections
  Non adiabatic dynamics: MD with Quantum Jumps Tully ('90)

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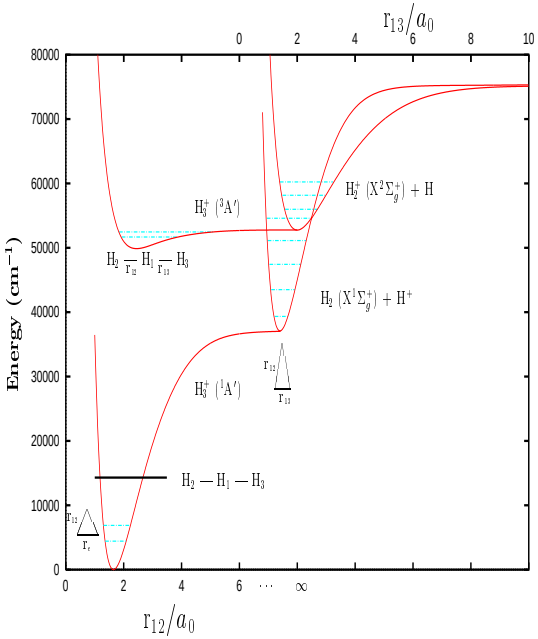
H_n^+: Potential energy surfaces

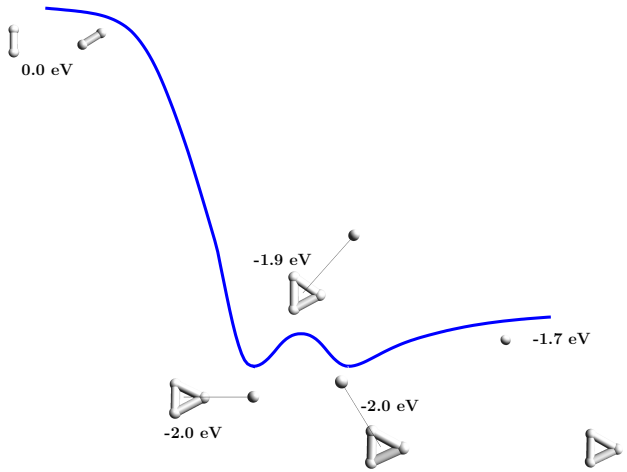
$$H^+ + H_2 \rightarrow H_2 + H^+$$



3 Dimensions

Aguado, et al.('00)

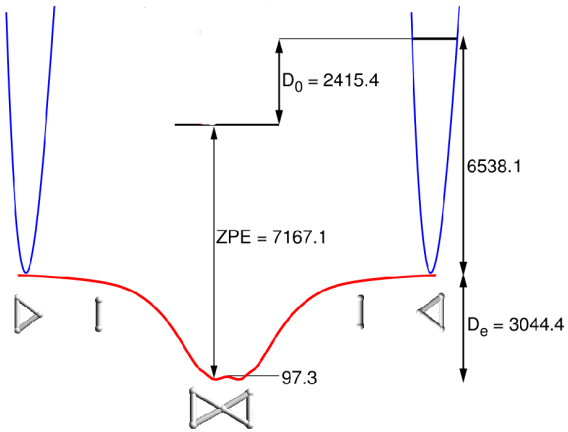
$$H_2^+ + H_2 \rightarrow H_3^+ + H$$



6 Dimensions

Sanz-Sanz, et al.('13)

$$H_3^+ + H_2 \rightarrow H_2 + H_3^+$$



9 Dimensions

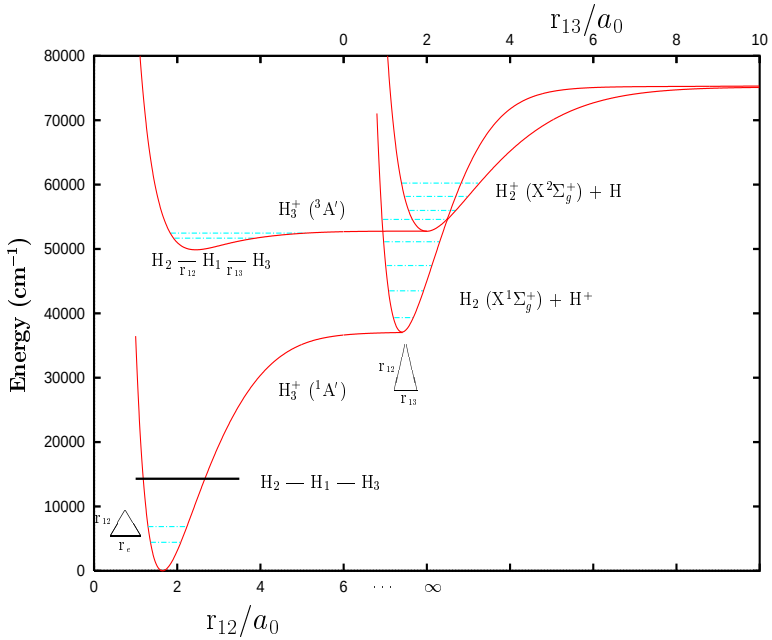
Aguado, et al.('10)

- Proton exchange reaction: multistate problem
- Long interaction to describe low temperature

Fitting procedure for H_n^+

Need of Multiple Surface to describe charge transfer

- H_3^+: $V = H_{DIM} + V_{3B}$ Aguado *et al* (2000)
  - Long range behavior: Charge-quadrupole & induced dipole in diagonal of DIM matrix Velilla *et al* (2008)
  - Coupled diabatic PES's: 3-body terms in DIM matrix Varandas & co. (2007)



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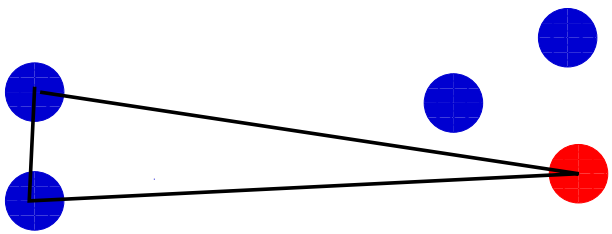
  - Long range behavior: Charge-quadrupole & induced dipole in diagonal of DIM matrix Velilla *et al* (2008)
  - Coupled diabatic PES's: 3-body terms in DIM matrix Varandas & co. (2007)
- H_4^+ & H_5^+: $V = H_{TRIM} + V_{NB}$

$$\hat{H}_{TRIM}(i) = \sum_{n>i,o>n} \hat{H}^+_{ino}(n-i, o-i) - 2\sum_{p>i} \hat{H}^+_{ip}(p-i)$$

Aguado et al.('10), Sanz et al. ('13)



- High accuracy in fitting
- Long range interaction
- Symmetric under permutation
- Accurate triatomic fragments
- Non-adiabatic couplings

Analytical derivatives: Hellmann-Feynman theorem

Derivating electronic Schrödinger Eq. $\frac{\partial}{\partial\alpha}\left(H\phi_n\right) = \frac{\partial}{\partial\alpha}\left(W_n\phi_n\right)$

and premultiplying by $\phi_{n'}$ and integrating

$$\left\langle \phi_{n'} \left| \frac{\partial H}{\partial\alpha} \right| \phi_n \right\rangle = \delta_{nn'}\frac{\partial W_n}{\partial\alpha} + \left(1-\delta_{nn'}\right)\left(W_n - W_{n'}\right)\left\langle \phi_{n'} \left| \frac{\partial\phi_n}{\partial\alpha} \right\rangle \right.$$

$$\phi_n = \sum_d T_n^d f_d \quad \rightarrow \quad \left\langle \phi_{n'} \left| \frac{\partial\phi_n}{\partial\alpha} \right\rangle \right. = \sum_{dd'} \frac{\left(T_{n'}^{d'}\right)^\dagger T_n^d}{W_n - W_{n'}} \frac{\partial\langle f_{d'}|H|f_d\rangle}{\partial\alpha}$$

where $\langle f_{d'}|H|f_d\rangle$ are the matrix elements of the TRIM Hamiltomian

Analytical: potential derivatives non-adiabatic matrix elements for H_3^+, H_4^+ & H_5^+

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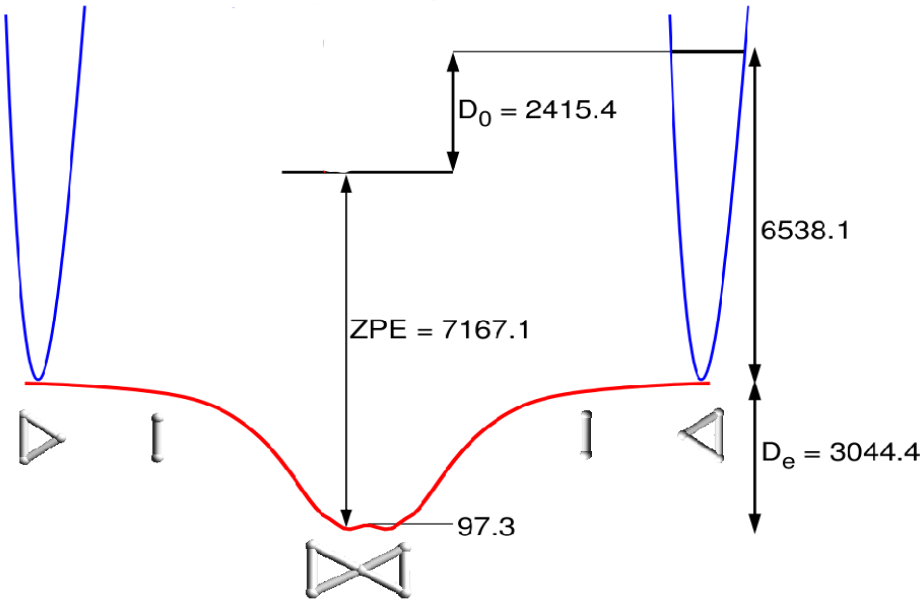
$H_3^+ + H_2 \rightarrow H_2 + H_3^+$ exchange reaction

- Production of H_2D^+
- Ortho/para conversion of H_3^+
- Large Zero Point energy

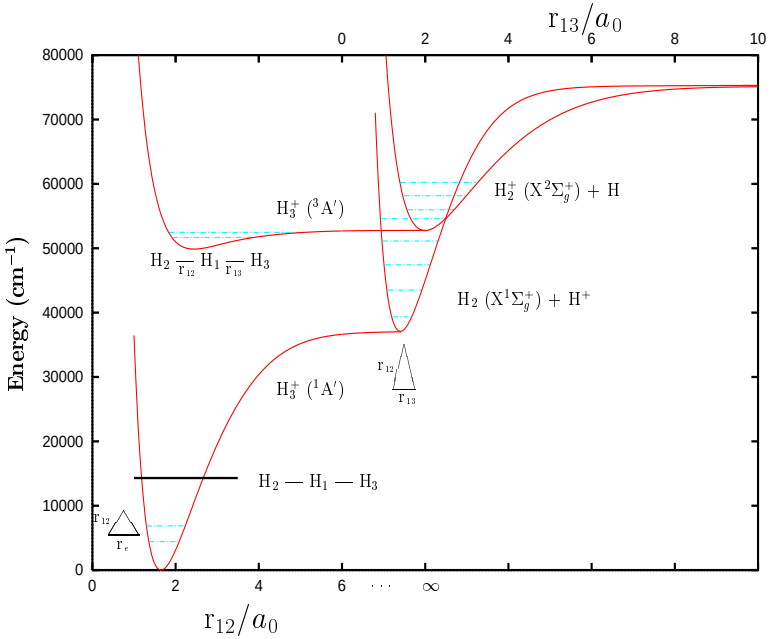


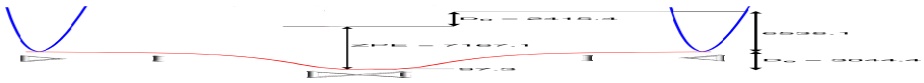
$$
\begin{aligned}
(HHH)^+ + HH &\rightarrow (HHH)^+ + HH && \text{inelastic} \\
&\rightarrow HH + (HHH)^+ && \text{hop : } \quad 3\,\text{channels} \\
&\rightarrow HH + (HHH)^+ && \text{exchange : } \quad 6\,\text{channels}
\end{aligned}
$$

Each pathway obeys strict nuclear spin selection rules Cordonnier et al. ('00)

This allows to "infer" the hop/exchange ratio: $\alpha = k^H/k^E$ Crabtree et al. ('11)

$H_3^+ + H_2 \rightarrow H_2 + H_3^+$ exchange reaction





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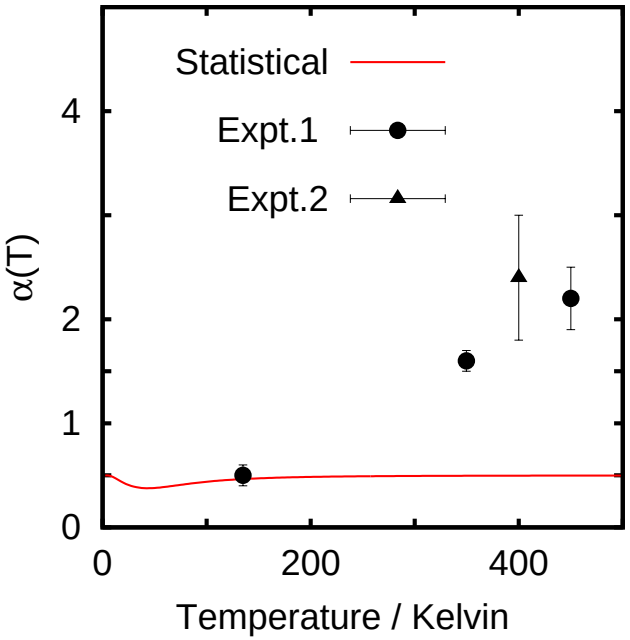
hop/exchange ratio, α, and statistical behaviour



α inferred from observed p-H_3^+ fraction vs. p-H_2 enrichment

Expt. 1: Crabtree et al. JCP ('11)
Expt. 2: Cordonnier et al. JCP ('00)

H_5^+ complex lives enough to allow full scrambling

Statistical limits: Parker& Light('07), Hugo *et al.*('09)

- no scrambling $S_M = \{1/4, 3/4, 0\}$ $\alpha = \infty$
- full scrambling $S_M = \{1/10, 3/10, 6/10\}$ $\alpha =$0.5

Need of dynamics to describe transition

Beyond Pure Statistical Models

- Need of dynamics to describe α transition

  - Many degree of freedom (10D)
  - Low energy and long-lived resonances
  - All atoms are equivalent: NO reduced dimension models
  - Quantum and many semiclassical methods difficult

- Introduce dynamical Bias through determination of S_M using Quassi-classical trajectories

González-Carrasco et . al. JCP **137**, ('12), 094303

H_2+ H_3^+: Statistical model of Park & Light, JCP ('07)

For total angular momentum, J, and nuclear spin, I, the reaction probability

$$P^{JI\Omega}_{sr,M's'r'}(E) = \frac{g_{Is}\,\gamma^{M'}_{sIs'}\,W^{J\Omega}_{sr\nu\Omega_t}(E)\,W^{J\Omega}_{s'r'\nu'\Omega'_t}(E)}{\sum''\gamma^{M''}_{sIs''}\,W^{J\Omega}_{s''r''\nu''\Omega''_t}(E)}$$

1. Nuclear spin statistical weight matrix, g
2. Capture probability, $W^{J\Omega}_{sr\nu\Omega_t}$
3. Spin branching ratio matrices, $\gamma^{M'}_{sIs'}$
4. Scrambling matrix, $S_M = \{1/10, 3/10, 6/10\}$

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1. Nuclear spin statistical weight matrix, g
2. Capture probability, $W^{J\Omega}_{sr\nu\Omega_t}$
3. Spin branching ratio matrices, $\gamma^{M'}_{sIs'}$
4. Scrambling matrix, S_M from dynamical calculations

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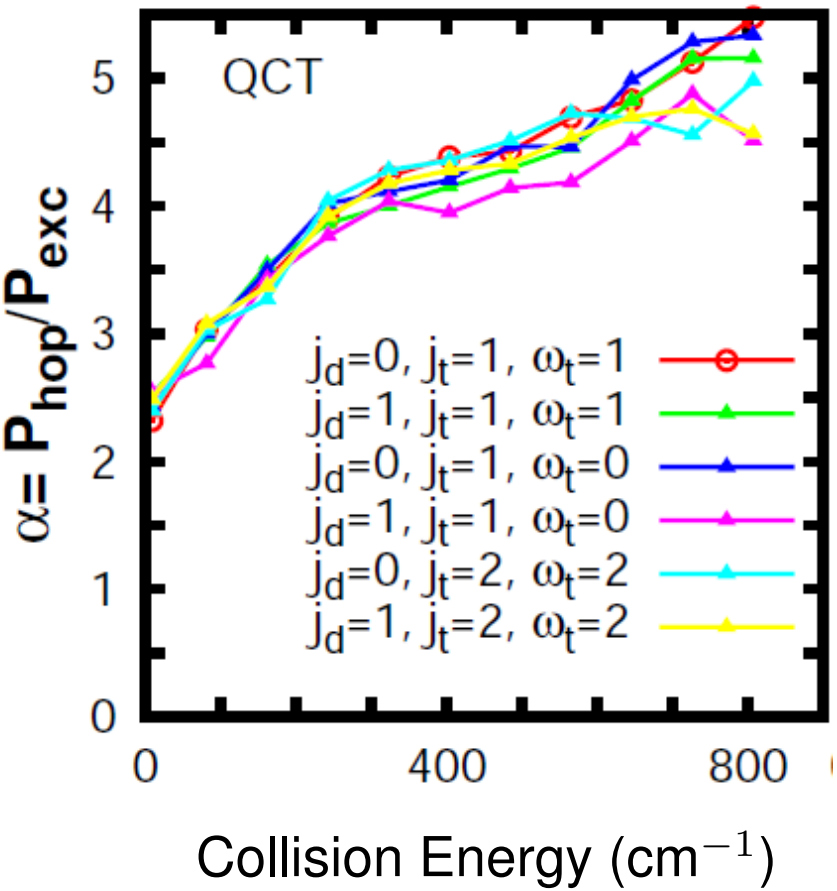
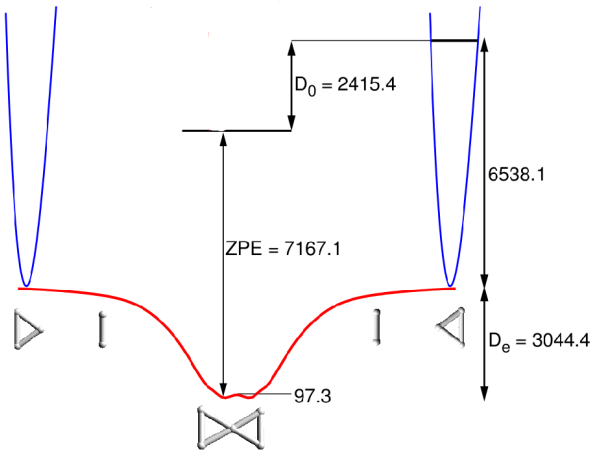
QCT Dynamically biased S_M and ZPE

$S_M(E)$ = QCT prob.



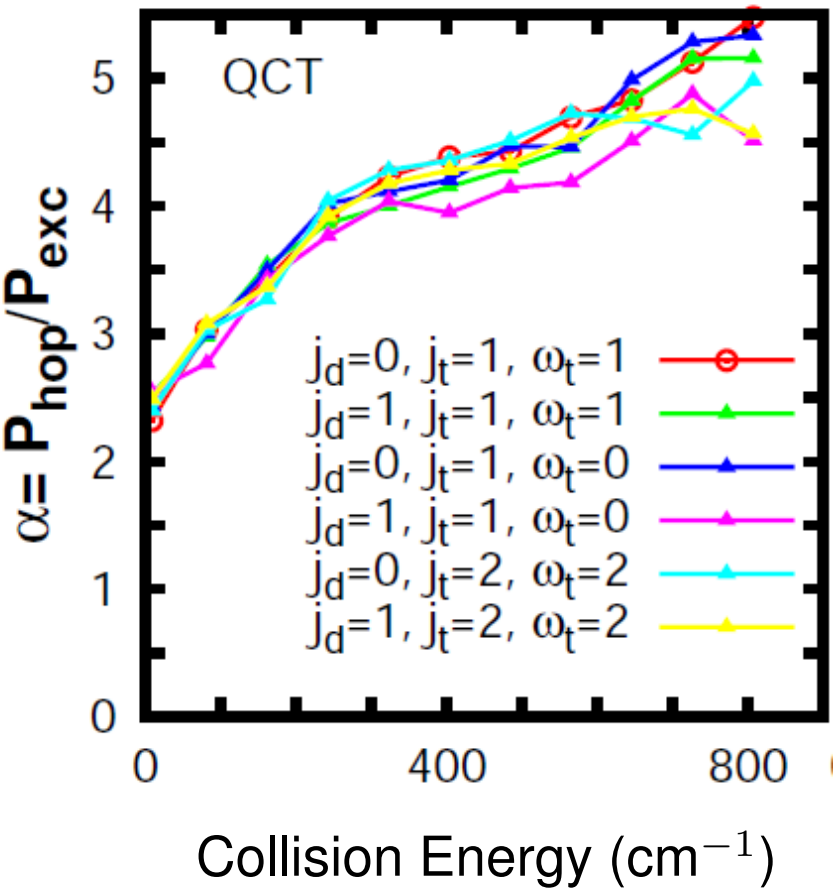


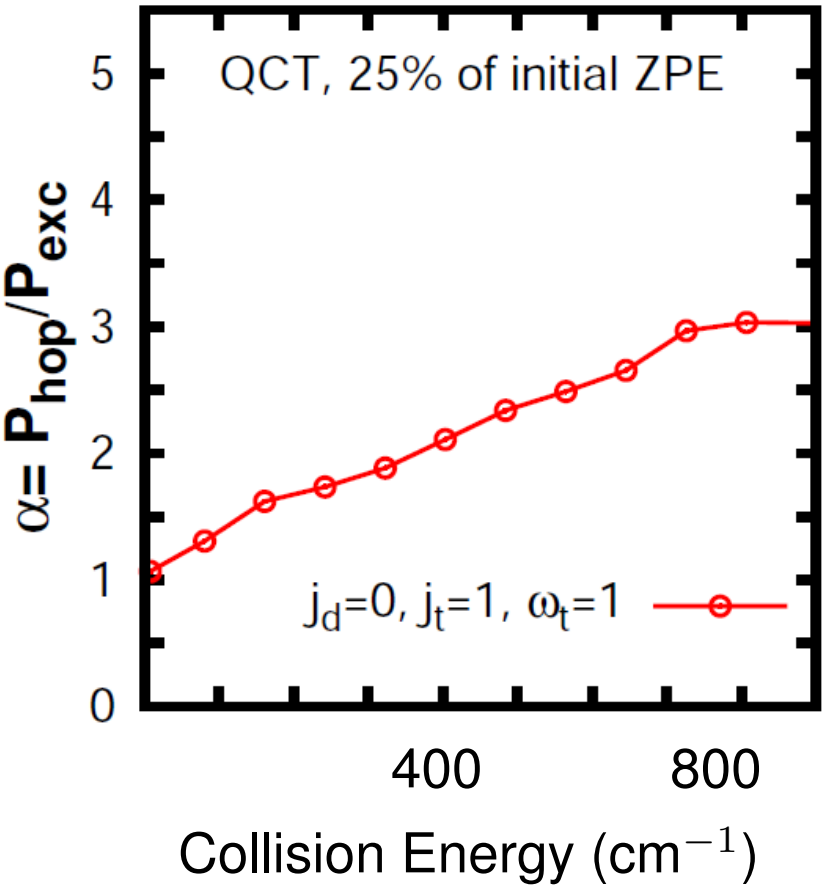
- α too high!!
- ZPE favors direct hop mechanism

QCT Dynamically biased S_M and ZPE

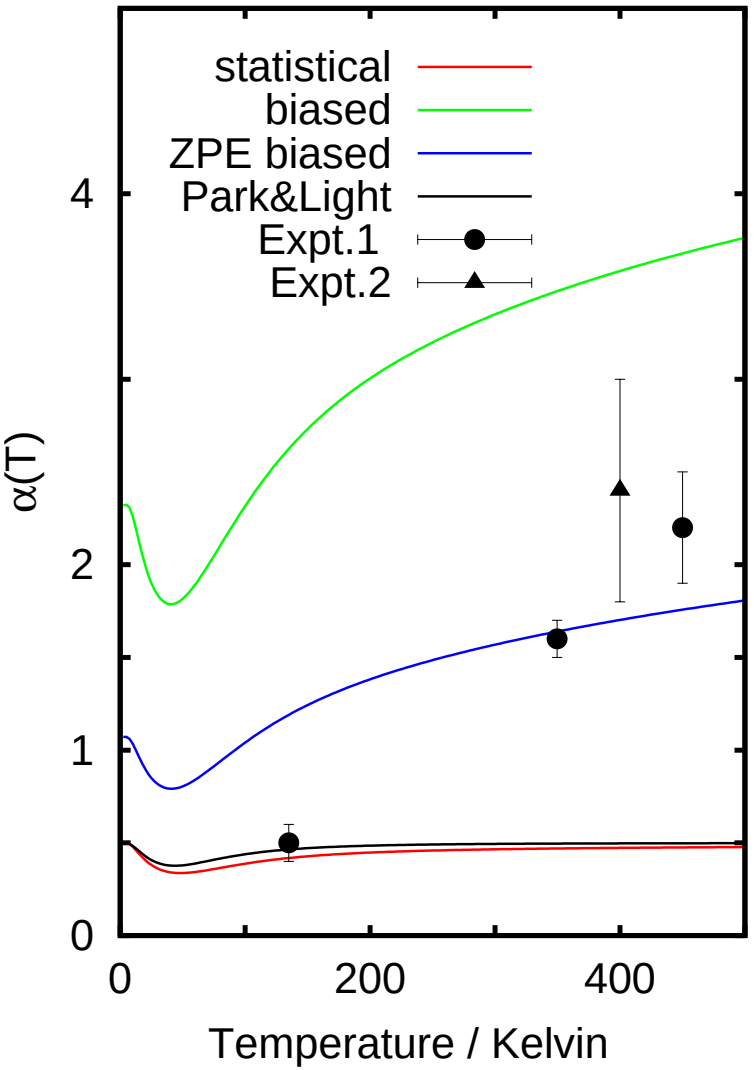
$S_M(E)$ = QCT prob. $\text{ZPE}_{H_2} + \text{ZPE}_{H_3^+} = 6538 \approx \text{ZPE}_{H_5^+} = 7167\ \text{cm}^{-1}$

ZPE reduction: Manikandan & Hase ('12)





Comparison with Experiments



Expt. 1: Crabtree, *et al.*, J. Chem. Phys.,**134**,('11)
Expt. 2: Cordonnier, *et al.*, J. Chem. Phys.,**113**,('00)
Simul. Gómez-Carrasco *et al* J. Chem. Phys.,('12)

- ZPE plays a fundamental role
- ZPE-biased "works" at T $>$ 300 K
- Statistical behaviour at T$<$ 200 K
- Need of quantum treatments
- Direct experimental information in infrared predissociation spectra

Experiments by Cheng et al. JPCl ('10)

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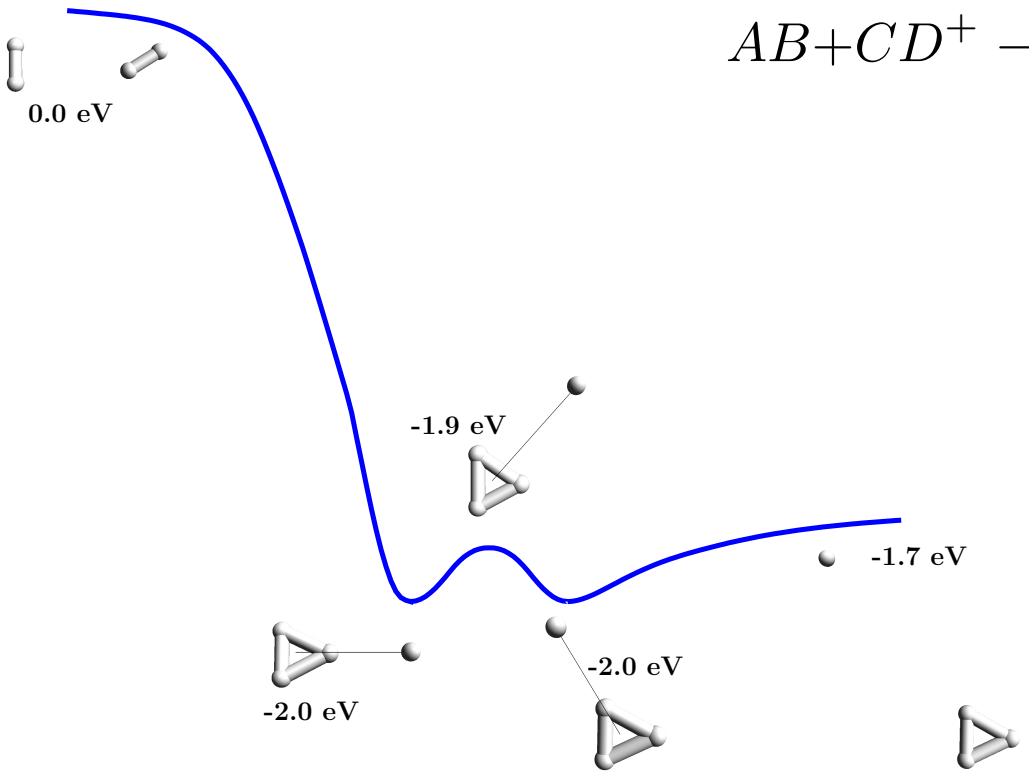
Direct H_2+ $H_2^+ \rightarrow$ H + H_3^+ reaction

Total reaction cross section using QCT



AB+$CD^+ \rightarrow$

$A + BCD^+$
$B + ACD^+$
} atom hop

$ABC^+ + D$
$ABD^+ + C$
} proton hop

AB+$CD^+ \rightarrow$ identity

$AC + BD^+$
$AC^+ + BD$
$AD + BC^+$
$AD^+ + BD$
} exchange

Direct H_2+ $H_2^+ \rightarrow H + H_3^+$ reaction

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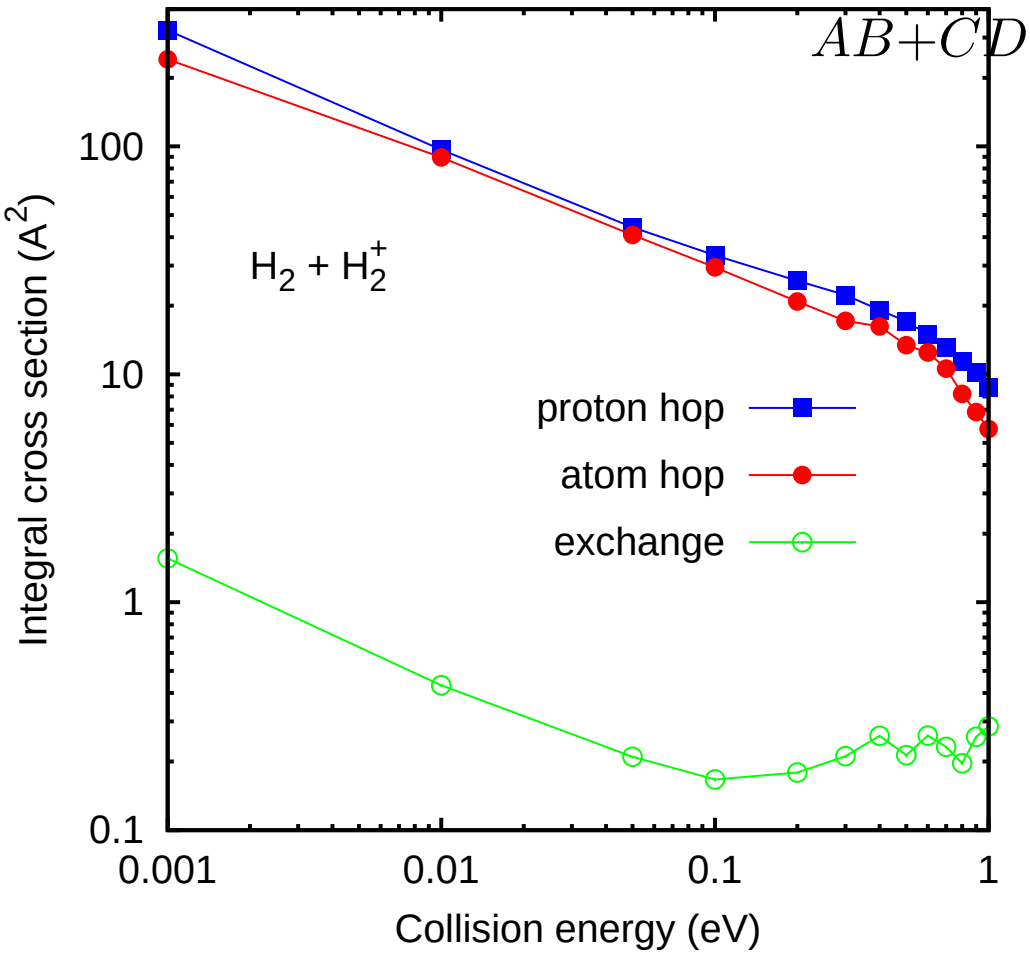

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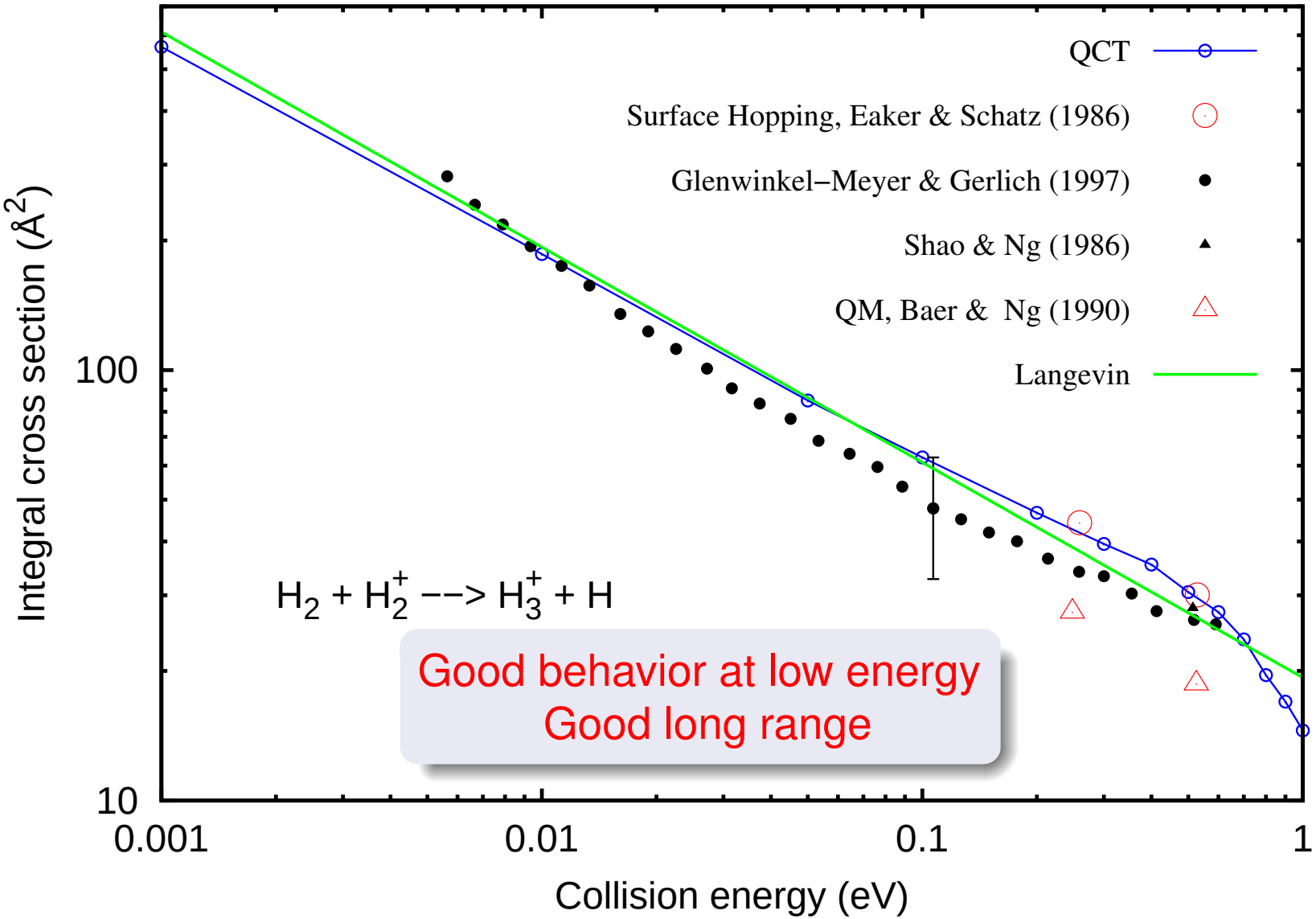
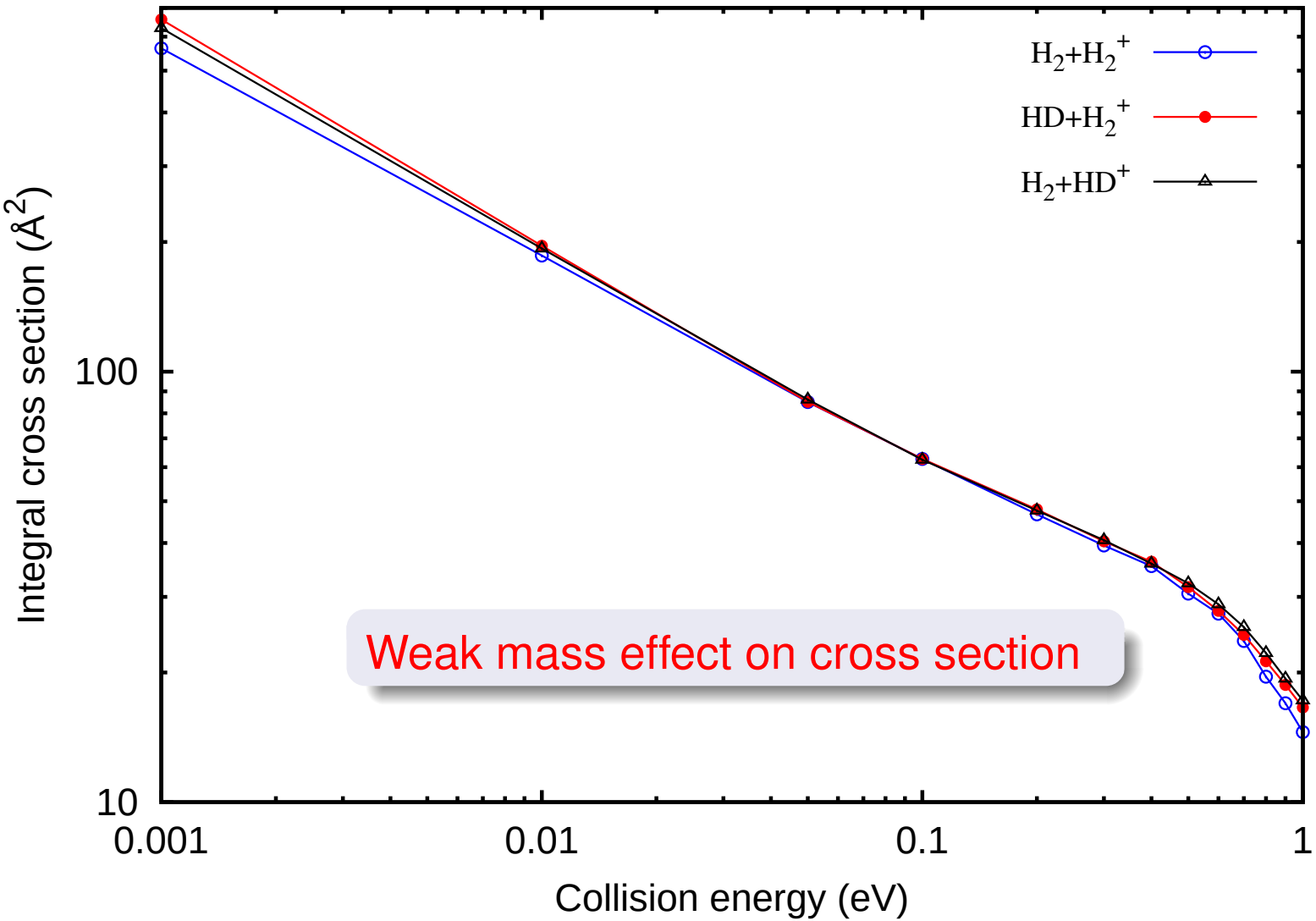
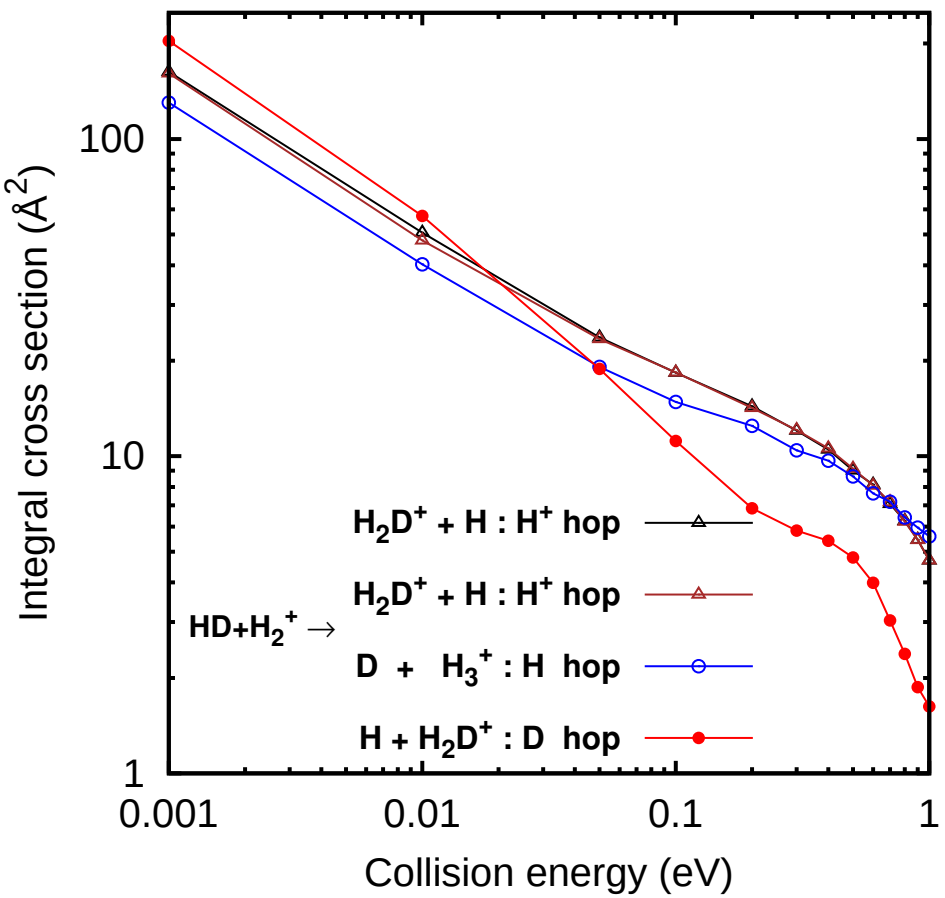


Good behavior at low energy
Good long range

Deuterium effect on cross sections



H_2D^+ /H_3^+ ratio: D or H hop?



- More reaction channels → H_2D^+
- H_2^+ breaks more easily
- Variation of H-hop vs. D-hop

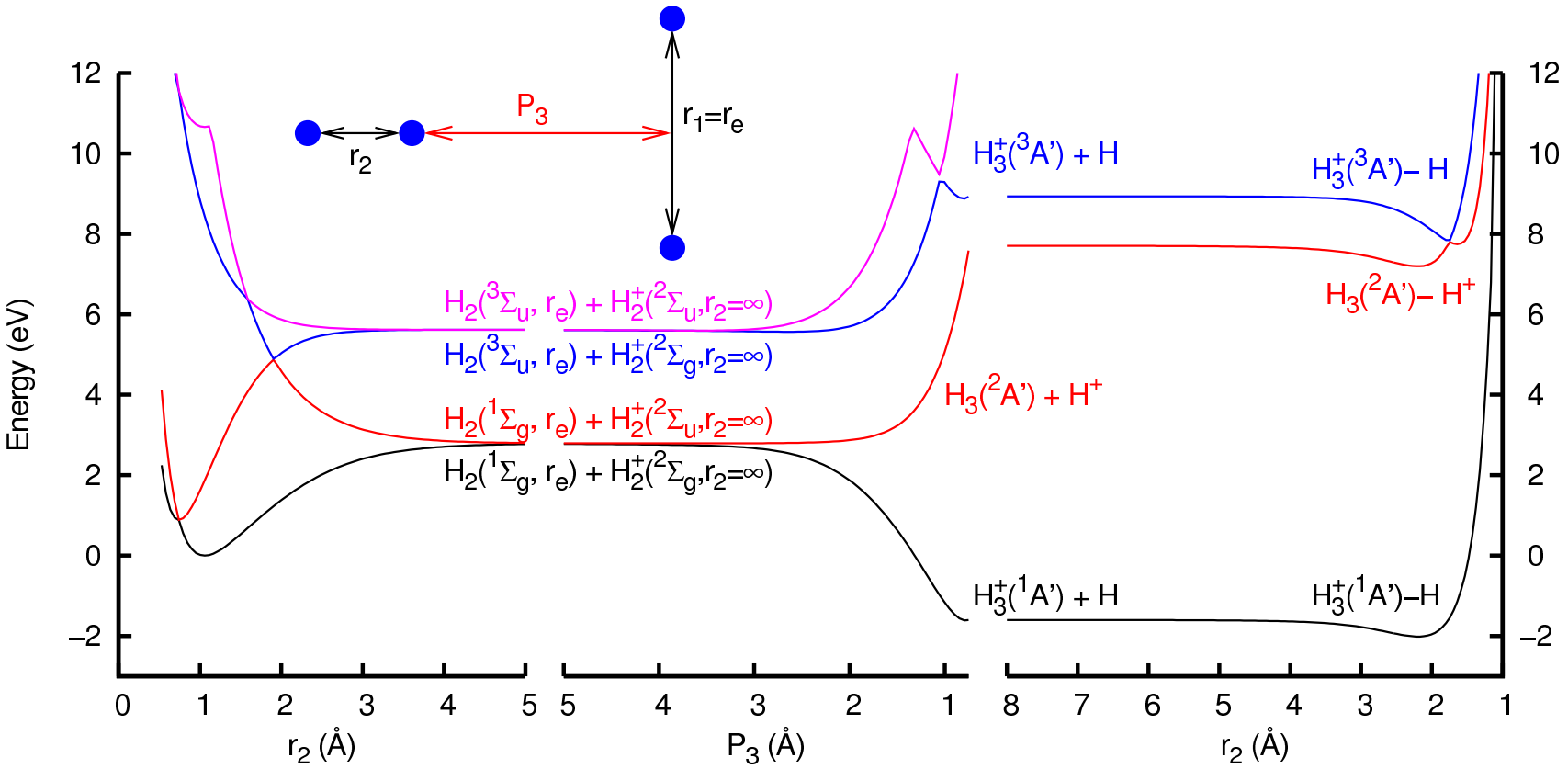
  density of states:
  $\rho(H_2D^+) > \rho(H_3^+)$

Quantum effects ?

- Nuclear spin and symmetry effects ?

Non-adiabatic vs charge transfer processes

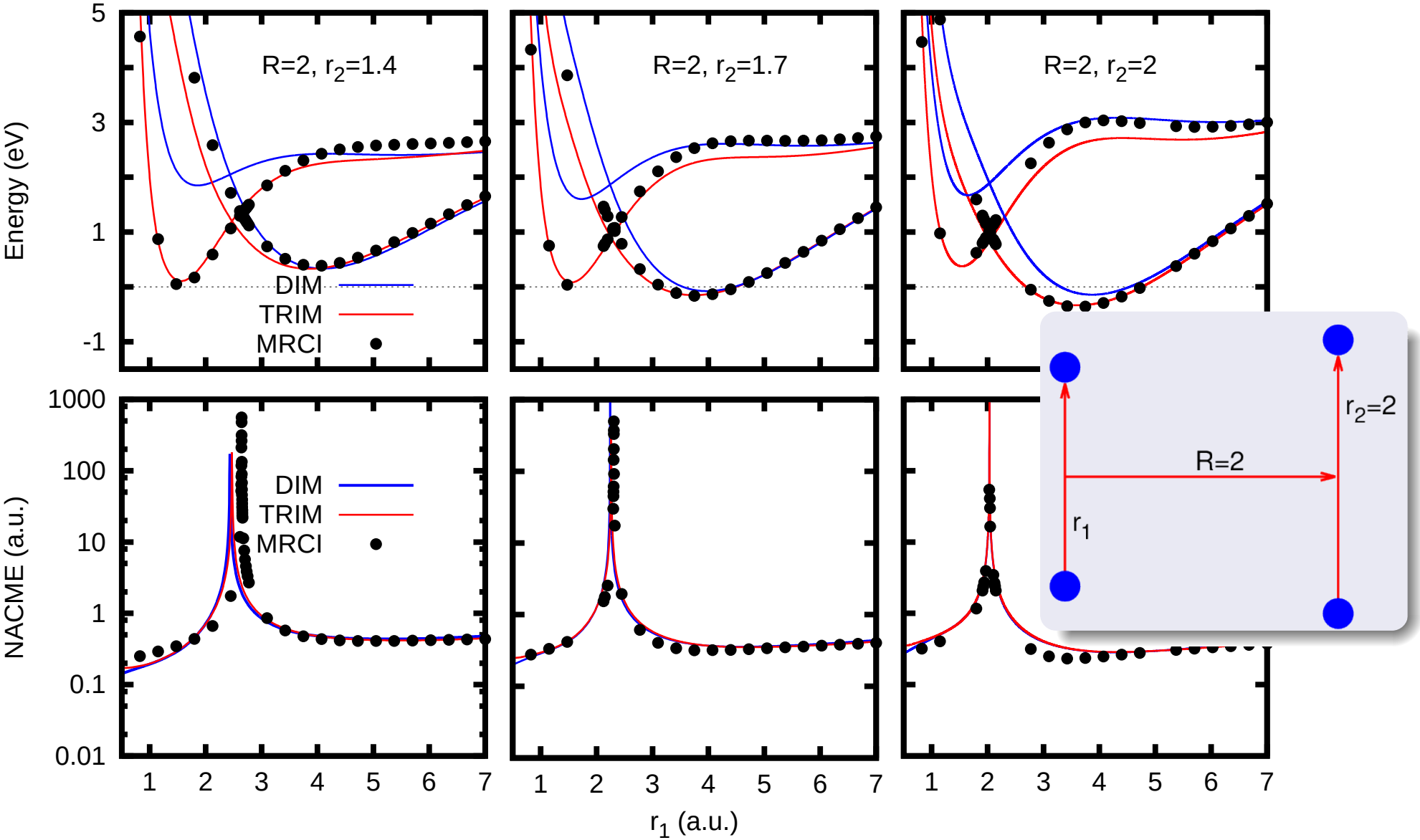
Crossings: when hydrogen atoms are at equivalent possitions



Sanz-Sanz et al. JCP ('13)

Stein & Muckerman, JCP,**68**('78)

Non-adiabatic couplings & Conical intersections



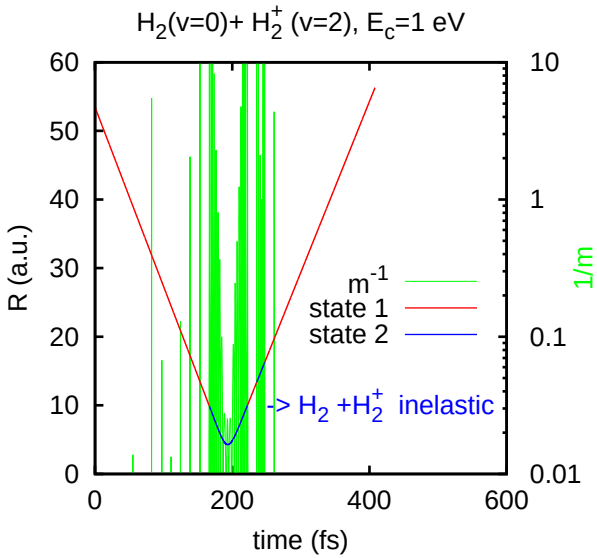
Non-adiabatic dynamics

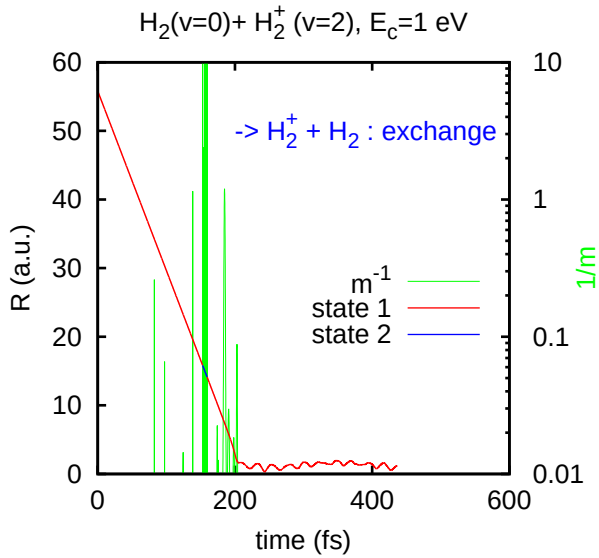
Using the "Molecular dynamic with quantum jumps" method (Tully '90)

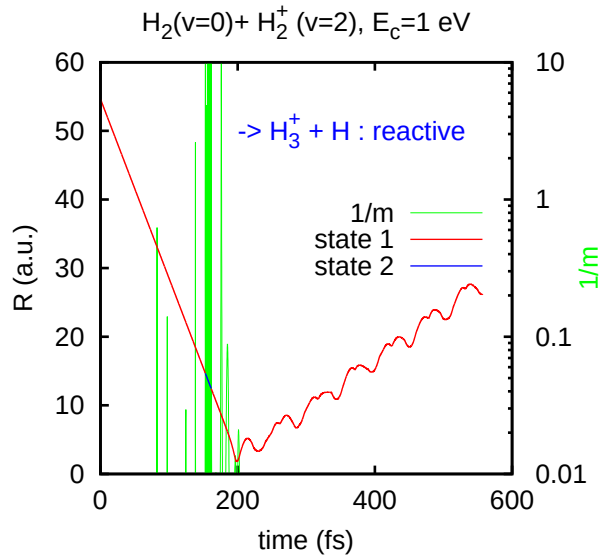
with 2 adiabatic states

Transitions proportional to the inverse of Masey parameter:

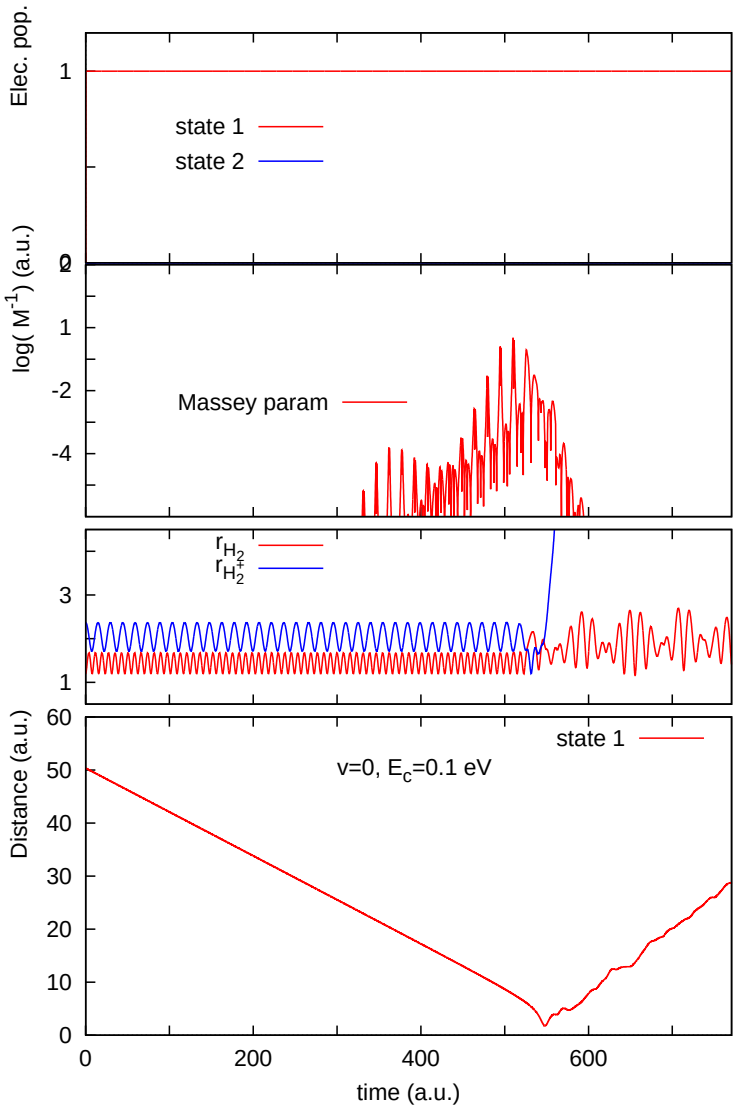
$$m_{ij}^{-1} = \frac{\vec{v} \cdot \vec{\nabla}_{ij}}{2\left(W_i - W_j\right)}$$







Surface hopping method (Tully)



- Electronic Quantum Wave packet

$$\Phi(t) = a_1(t)|1\rangle + a_2(t)|2\rangle$$

Split Operator propagator

- "Electronic jumps" probability

Proportional $\partial a_i(t)/\partial t$

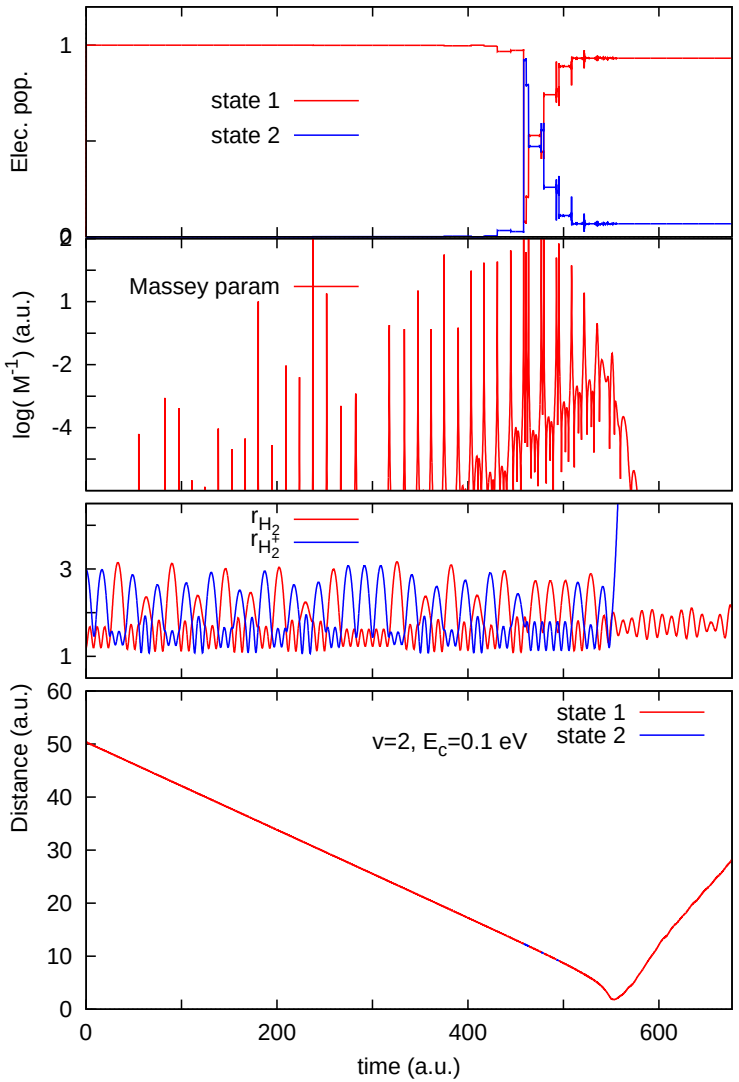
- Classical trayectory on $|1\rangle$ or $|2\rangle$

Energy change along ∇_{ij}

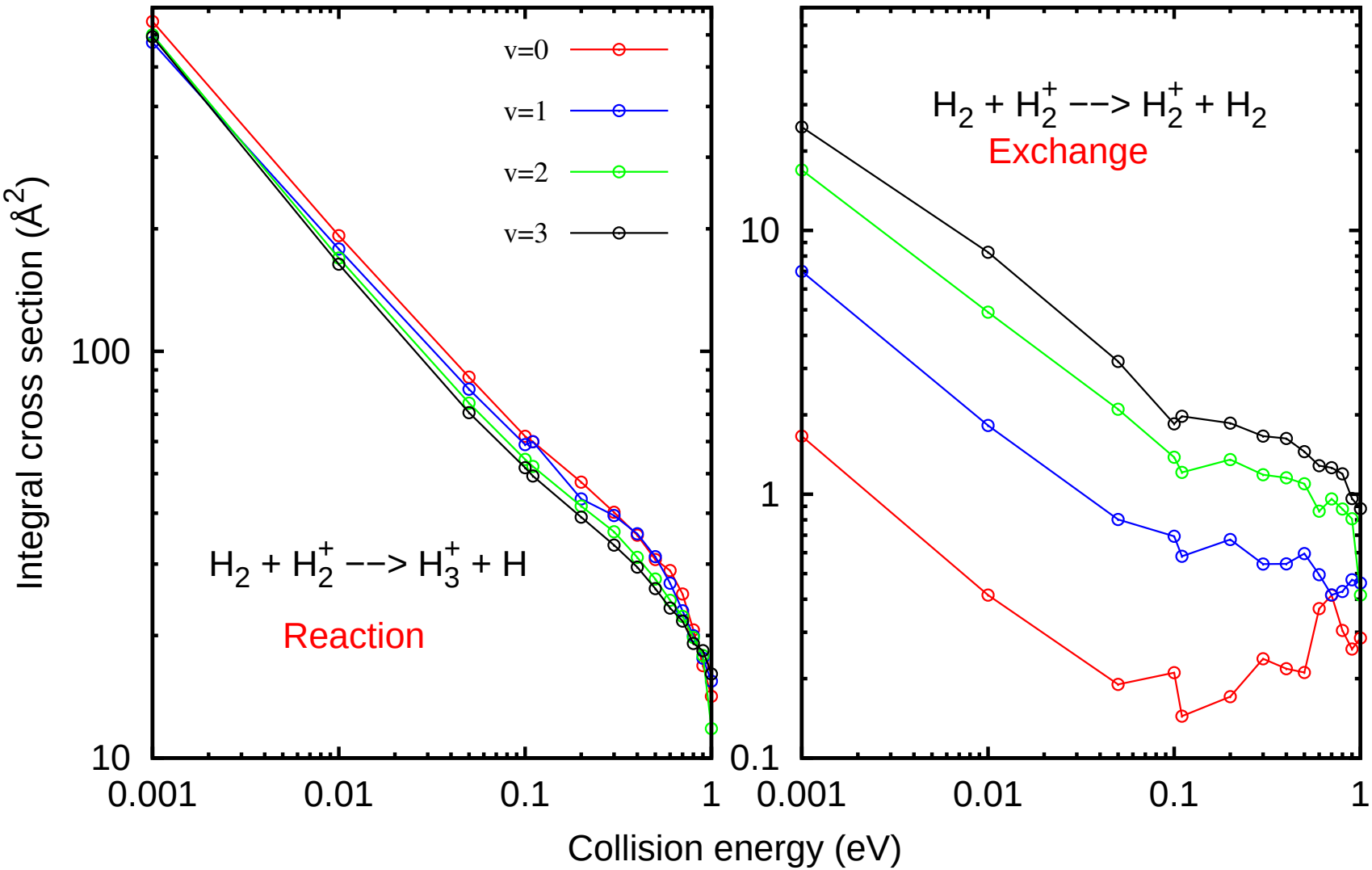
Example v=0 and 2 for E_c=0.1 eV

Surface hopping method (Tully)

Is adiabatic approach good?

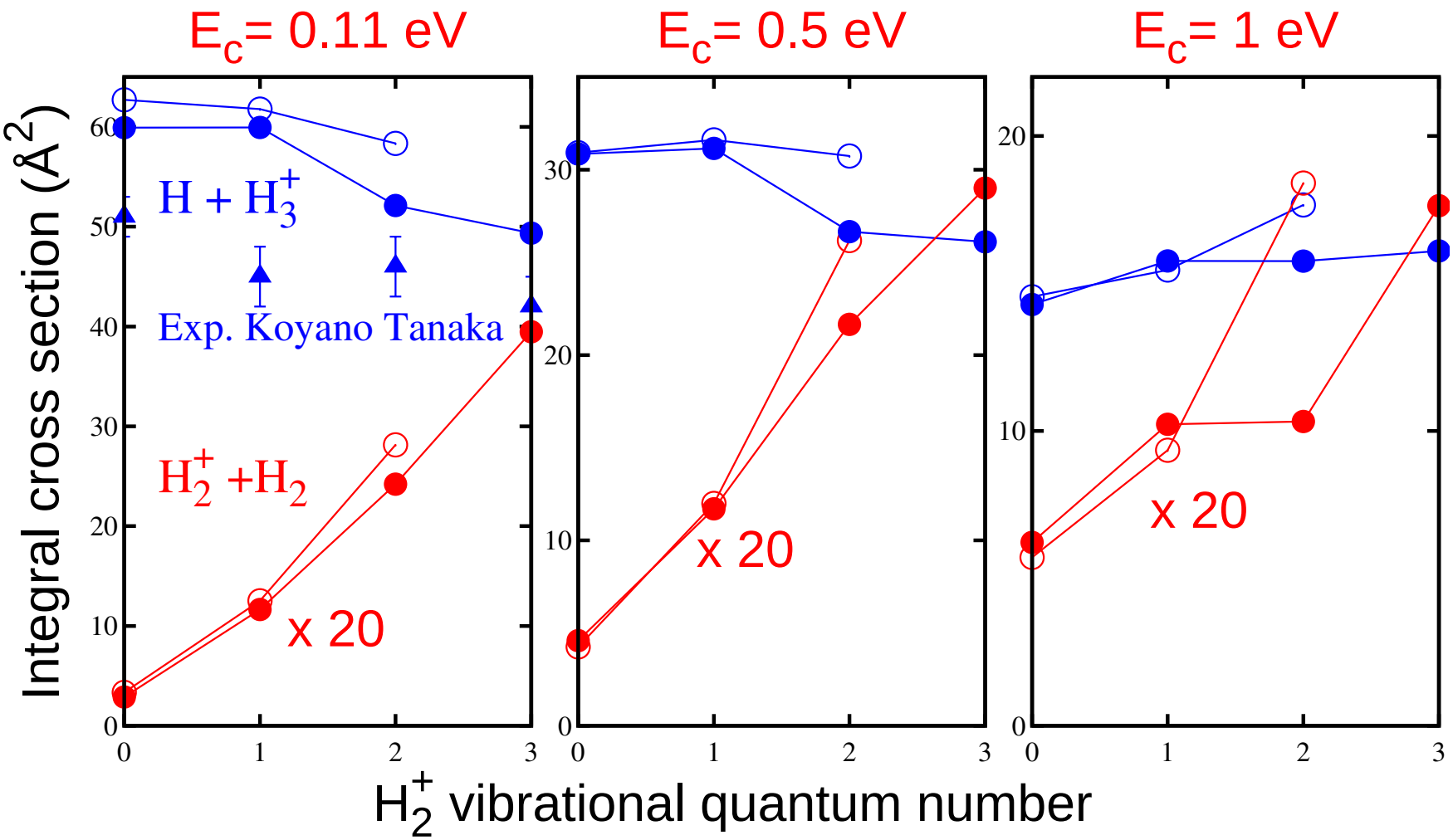


Initial vibration effect



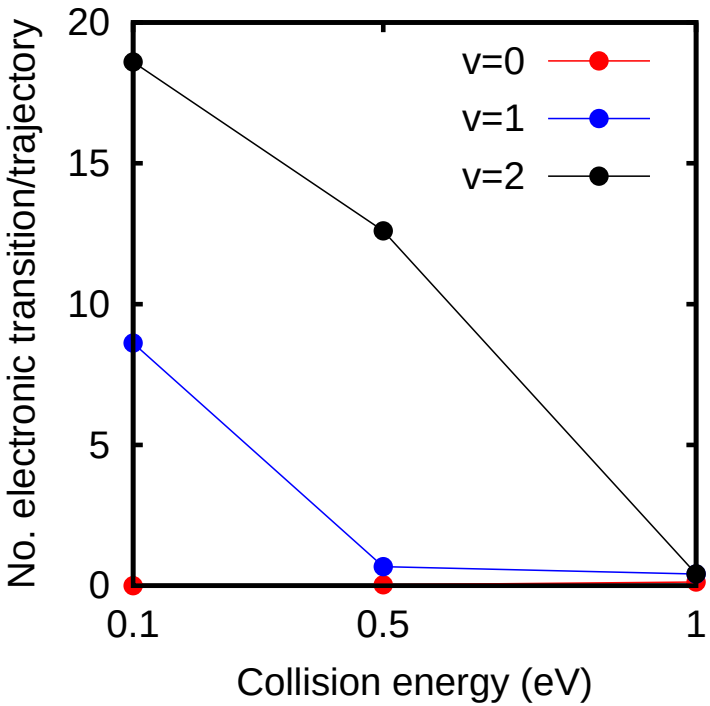
Initial vibration effect

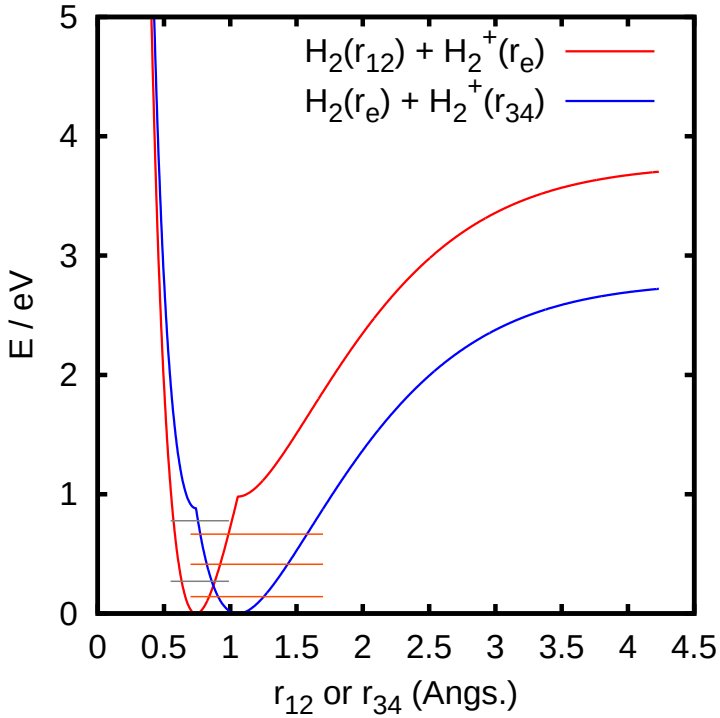
$H_2 + H_2^+(v) \rightarrow$



Triangles: Experiments at 0.11 eV by Koyano & Tanaka, JCP('80)
open circles: QCT full circles: Surface hopping with 2 states

Collision energy effect





Outline

1. Introduction
2. H_n^+ PES's
3. H_2+H_3^+ exchange reaction
4. H_2+H_2^+ direct reaction
5. Conclusions

Conclusions ?

- Accurate analytical PES of H_4^+ and H_5^+ based on a TRIM description, with analytic derivatives and NACME

- H_2+ H_3^+ collisions presents a transition from statistical behaviour at T< 200K and a more direct mechanism at T> 300 K.
  Need of Quantum methods to study this transition & to understand the statistical behaviour at low temperatures, due to long-lived resonances

- H_2+$H_2^+(v=0) \rightarrow H_3^+$+H is a direct reaction, well described on a single surface for $E_{col} < 1$ eV.
- For $v > 0$, non-adiabatic processes are important, specially at low E_c
- The TRIM based PES describes accurately H_3^+ fragments: need of quantum methods and nuclear spin statistics to describe final H_3^+ rovibrational states

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