Reactions involving the formation and transformation of $\text{H}_3^+$

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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**

**Introduction**

- $H_2^+$ PES's
- $H_2 + H_3^+$ exchange reaction
- $H_2 + H_2^+$ direct reaction
- Conclusions

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

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

- **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

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Chemical pumping in molecular clouds and PDR’s

- Exothermic reactions of $\text{H}_2$ with atoms and ions
  \[ H_2(v = 0) + O^+ \rightarrow OH^+(v', j') + H \]

- Chemistry of $\text{H}_2(v > 0)$ in ISM

  **Initial state dependent chemistry**

  \[ H_2(v = 1) + C^+ \rightarrow CH^+(v', j') + H \]

  \[ H_2(v > 1) + S^+ \rightarrow SH^+(v', j') + H \]
  Zanchet, et al. AJ, 146,125 ('13)
Chemical pumping in molecular clouds and PDR’s

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  \[ \text{H}_2(v = 0) + O^+ \rightarrow \text{OH}^+(v', j') + \text{H} \]

- Chemistry of $\text{H}_2(v > 0)$ in ISM

- Initial state dependent chemistry
  \[ \text{H}_2(v = 1) + C^+ \rightarrow \text{CH}^+(v', j') + \text{H} \]
  \[ \text{H}_2(v > 1) + S^+ \rightarrow \text{SH}^+(v', j') + \text{H} \]
  Zanchet, et al. AJ, 146, 125 ('13)

- The most abundant ion is $\text{H}_3^+$
  - $\text{H}_2^+$ disappears rapidly in the exothermic $\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$ reaction
  - However $\text{H}_2 + \text{H}_3^+ \rightarrow \text{H}_3^+ + \text{H}_2$ (ortho/para conversion, deuteration)
  - $\text{H}_3^+$ is very reactive with other species:
    \[ \text{H}_3^+ + O \rightarrow \text{H}_2 + \text{OH}^+ \]
    \[ \text{H}_3^+ + \text{O}_2 \rightarrow \text{H}_2 + \text{O}_2\text{H}^+ \]
Chemical pumping in molecular clouds and PDR’s

- Exothermic reactions of $\text{H}_2$ with atoms and ions
  \[
  \text{H}_2(v = 0) + \text{O}^+ \rightarrow \text{OH}^+(v', j') + \text{H}
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  \]
  Zanchet, et al. AJ,146,125 ('13)

- The most abundant ion is $\text{H}_3^+$
  - at low T molecules freeze
  - $\text{H}_3^+$ “lives” longer time
  - $\text{H}_3$ Deuteration occurs
  - Key process for high D/H

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Previous studies on $H^+_4$.

- **Experimental**
  \[ H_2 + H_2^+ (v = 0 - 3) \rightarrow H_3^+ + H \text{ and isotopic variants} \]
  Koyano & Tanaka ('80); Anderson et al. ('81), Krenos et al. ('76), ...
  $H_3^+$ infrared spectra, produced in the previous 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)
Introduction

H⁺ PES’s
H₂+H₃⁺ exchange reaction
H₂+H₂⁺ direct reaction

Conclusions

Objectives

- Full dimensional PES for H⁺₄ and H⁺₅
  - with good long range behavior
  - with analytical derivatives and non-adiabatic couplings

H₂+ H⁺₃ → H⁺₃+H₂  Is the reaction statistical?:

Going beyond pure statistical approach
- Introduction of dynamical bias
- Use global PES
Comparison with experimental Kₜıp/K tua

H₂+ H⁺₂ → H⁺₃+H

Non adiabatic couplings and Conical intersections
Non adiabatic dynamics: MD with Quantum Jumps

Parker & Light (’07), Hugo et al. (’09)

McNab and coworkers (’11)

Tully (’90)
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**H**$_n$**: Potential energy surfaces

\[ H^+ + H_2 \rightarrow H_2 + H^+ \]

\[ H_2^+ + H_2 \rightarrow H_3^+ + H \]

\[ H_3^+ + H_2 \rightarrow H_2 + H_3^+ \]

- **3 Dimensions**
  Aguado, et al. (’00)

- **6 Dimensions**
  Sanz-Sanz, et al. (’13)

- **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

- $H^+_3$: $V = H_{DIM} + V_{3B}$
  - Long range behavior: Charge-quadrupole & induced dipole in diagonal of DIM matrix
  - Coupled diabatic PES’s: 3-body terms in DIM matrix

Aguado et al. (2000)

Velilla et al. (2008)

Varandas & co. (2007)
Fitting procedure for $H_n^+$

Need of Multiple Surface to describe charge transfer

- $H_3^+$: $V = H_{DIM} + V_{3B}$  
  - Long range behavior: Charge-quadrupole & induced dipole in diagonal of DIM matrix  
  - Coupled diabatic PES’s: 3-body terms in DIM matrix  

- $H_4^+ \& H_5^+$: $V = H_{TRIM} + V_{NB}$  
  - High accuracy in fitting  
  - Long range interaction  
  - Symmetric under permutation  
  - Accurate triatomic fragments  
  - Non-adiabatic couplings

Aguado et al. (2000)

Velilla et al. (2008)

Varandas & co. (2007)

Aguado et al. (’10), Sanz et al. (’13)
Analytical derivatives: Hellmann-Feynman theorem

Deriving electronic Schrödinger Eq.

\[ \frac{\partial}{\partial \alpha} (H \phi_n) = \frac{\partial}{\partial \alpha} (W_n \phi_n) \]

and premultiplying by \( \phi_n' \) and integrating

\[
\langle \phi_n' | \frac{\partial H}{\partial \alpha} | \phi_n \rangle = \delta_{nn'} \frac{\partial W_n}{\partial \alpha} + (1 - \delta_{nn'}) (W_n - W_{n'}) \langle \phi_n' | \frac{\partial \phi_n}{\partial \alpha} \rangle
\]

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

where \( \langle f_{d'} | H | f_d \rangle \) are the matrix elements of the DIM or TRIM Hamiltonian

Analytical: potential derivatives
non-adiabatic matrix elements
for \( H_3^+, H_4^+ \) & \( H_5^+ \)
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**H$_3^+$ + H$_2$ → H$_2$ + H$_3^+$ exchange reaction**

- Production of H$_2$D$^+$
- Ortho/para conversion of H$_3^+$
- Large Zero Point energy

\[
\begin{align*}
&(H H H)^+ + HH \rightarrow (H H H)^+ + HH \\
&\quad\quad\quad \rightarrow HH + (H H H)^+ \\
&\quad\quad\quad \rightarrow HH + (H H H)^+ \\
\end{align*}
\]

Each pathway obeys strict **nuclear spin** selection rules

This allows to “infer” the hop/exchange ratio: \( \alpha = k^H / k^E \)

Cordonnier et al. ('00)  
Crabtree et al. ('11)

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$\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_3^+$ exchange reaction

\[(HHH)^+ + HH \rightarrow (HHH)^+ + HH\]  
\[\rightarrow HH + (HHH)^+\]  
\[\rightarrow HH + (HHH)^+\]

Each pathway obeys strict nuclear spin selection rules

This allows to "infer" the hop/exchange ratio: $\alpha = k^H / k^E$

Cordonnier et al. (’00)  
Crabtree et al. (’11)
**hop/exchange ratio, $\alpha$, and statistical behaviour**

\[ \alpha \text{ inferred from observed p-H}_3^+ \text{ fraction vs. p-H}_2 \text{ enrichment} \]

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:**

- 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 $\alpha$ 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

$$P_{sr,M's'r'}^{JI\Omega}(E) = \frac{g_{Is} \gamma_{sIs'}^{M'} W_{sr\nu\Omega t}^{J\Omega}(E) W_{s'r'\nu'\Omega t'}^{J\Omega}(E)}{\sum'' \gamma_{sIs''}^{M''} W_{sr\nu\Omega t}^{J\Omega}(E) W_{s'r'\nu'\Omega t'}^{J\Omega}(E)}$$

1. Nuclear spin statistical weight matrix, $g$

2. Capture probability, $W_{sr\nu\Omega t}^{J\Omega}$

3. Spin branching ratio matrices, $\gamma_{sIs'}^{M'}$

4. Scrambling matrix, $S_M = \{1/10, 3/10, 6/10\}$

$$(HHH)^+ + HH \rightarrow (HHH)^+ + HH \quad \text{inelastic}$$

$$\rightarrow HH + (HHH)^+ \quad \text{hop: 3 channels}$$

$$\rightarrow HH + (HHH)^+ \quad \text{exchange: 6 channels}$$
H$_2^+$ + H$_3^+$: Statistical model of Park & Light, JCP ('07)

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

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1. Nuclear spin statistical weight matrix, $g$

2. Capture probability, $W_{sr\nu\Omega_t}^J$

3. Spin branching ratio matrices, $\gamma_{sIs'}^M$

4. Scrambling matrix, $S_M$ from dynamical calculations

$$(HHH)^+ + HH \rightarrow (HHH)^+ + HH \quad \text{inelastic}$$

$$\rightarrow HH + (HHH)^+ \quad \text{hop: 3 channels}$$

$$\rightarrow HH + (HHH)^+ \quad \text{exchange: 6 channels}$$
QCT Dynamically biased $S_M$ and ZPE

$S_M(E) = \text{QCT prob.}$

- $\alpha$ too high!!
- ZPE favors direct hop mechanism
**QCT Dynamically biased $S_M$ and ZPE**

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

**ZPE reduction:** Manikandan & Hase (’12)

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**Figure:**

- **Left panel:** QCT plot with $\alpha = \frac{P_{\text{hop}}}{P_{\text{exc}}}$ vs. Collision Energy (cm$^{-1}$) for different values of $j_d, j_t, \omega_t$.
- **Right panel:** QCT, 25% of initial ZPE plot with $\alpha = \frac{P_{\text{hop}}}{P_{\text{exc}}}$ vs. Collision Energy (cm$^{-1}$).
Comparison with Experiments


- 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. JPCI (’10)
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Direct $H_2^+ + H_2^+ \rightarrow H + H_3^+$ reaction

Total reaction cross section using QCT

$AB + CD^+ \rightarrow A + BCD^+ \quad B + ACD^+$ \{ atom hop \}

$ABC^+ + D \quad ABD^+ + C$ \{ proton hop \}

$AB + CD^+ \rightarrow$ identity

$AC + BD^+ \quad AC^+ + BD \quad AD + BC^+ \quad AD^+ + BD$ \{ exchange \}

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**Introduction**

H$^+_n$ PES's

H$_2$H$_3^+$ exchange reaction

H$_2$H$_2^+$ direct reaction

**Conclusions**

Direct H$_2$ + H$_2^+$ $\rightarrow$ H + H$_3^+$ reaction

Total reaction cross section using QCT

![Graph showing cross section vs collision energy](image)

- **Integral cross section (Å$^2$)**
- **Collision energy (eV)**

\[ H_2 + H_2^+ \rightarrow \]

\[ A + BCD^+ \]
\[ B + ACD^+ \] \{ atom hop \}

\[ ABC^+ + D \]
\[ ABD^+ + C \] \{ proton hop \}

\[ AB + CD^+ \rightarrow \text{identity} \]

\[ AC + BD^+ \]
\[ AC^+ + BD \]
\[ AD + BC^+ \]
\[ AD^+ + BD \] \{ exchange \}

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Comparison with experiments

\[ \text{H}_2^+ + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H} \]

- QCT
- Surface Hopping, Eaker & Schatz (1986)
- Glenwinkel–Meyer & Gerlich (1997)
- Shao & Ng (1986)
- QM, Baer & Ng (1990)
- Langevin

Good behavior at low energy
Good long range
Deuterium effect on cross sections

Integral cross section (Å²) vs. Collision energy (eV)

- $H_2 + H_2^+$
- $HD + H_2^+$
- $H_2 + HD^+$

Weak mass effect on cross section
H$_2$D$^+$ /H$_3^+$ ratio: D or H hop?

- More reaction channels $\rightarrow$ H$_2$D$^+$
- H$_2^+$ breaks more easily
- Variation of H-hop vs. D-hop

\[
\rho(H_2D^+) > \rho(H_3^+)
\]

Classical effect?

- Nuclear spin and symmetry effects?
MEP of first electronic states

$H_2(1\Sigma_g^+, r_{el}) + H_2^+(2\Sigma_g^+, r_{el})$

$H_3^+(3\text{A}') + H(2\text{S})$

$H_3(1\text{A}') (\approx H_2(1\Sigma_g^+, H) + H^+)$

$H_2 + H_2^+$ ZPE $\approx 0.4$ eV

Crossing in the entrance channel

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Non-adiabatic vs charge transfer processes

Crossings: when hydrogen atoms are at equivalent positions

\[ \begin{align*}
H_2^+ + H_3^+ & \rightarrow H_3^+ + H^+ \\
H_2 + H_3 & \rightarrow H_3 + H^+ \\
H_2 + H_3 & \rightarrow H_3^+ + H
\end{align*} \]

Sanz-Sanz et al. JCP ('13)  
Stein & Muckerman, JCP, 68 ('78)

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Non-adiabatic couplings & Conical intersections

Energy (eV)

R=2, r_1 = 1.4
R=2, r_1 = 1.7
R=2, r_1 = 2

NACME (a.u.)

r_1 (a.u.)

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High symmetry: “diabolic points” (Yarkony)

linear structure $r_1=r_2=1.55$

square structure $r_1=r_2=2$

tetrahedric structure $r_1=2.4$, $r_2=2.4$

3 states CI

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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:

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

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Initial vibration effect on non-adiabatic dynamics

\[ \text{H}_2 + \text{H}_2^+(v) \rightarrow \]

![Graph showing integral cross section vs. \( \text{H}_2^+ \) vibrational quantum number for different energy thresholds.](image)

- **Triangles:** Experiments at 0.11 eV by Koyano & Tanaka, JCP('80)
- **Open circles:** QCT
- **Full circles:** Surface hopping with 2 states

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Collision energy effect

- Introduction
- \( H^+ \text{ PES's} \)
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<table>
<thead>
<tr>
<th>Collision energy (eV)</th>
<th>No. electronic transition/trajectory</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>20</td>
</tr>
<tr>
<td>0.5</td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
</tr>
</tbody>
</table>

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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 $T>300K$. 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 $E_{col}<1\text{ eV}$.
- 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
Acknowledgments

Collaborators

Cristina Sanz-Sanz, CSIC & Univ. Autónoma Madrid
Alfredo Aguado, Univ. Autónoma Madrid
Susana Gómez-Carrasco, Univ. Salamanca
Fedor Y. Naumkin, Univ. Toronto

Financial Support

Ministerio Ciencia y Tecnología (SPAIN)
CSD2009-00038, “Molecular Astrophysics: the Herschel and Alma era”
FIS2011-29596-C02