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

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QdB, Bilbao, July 13-14$^{th}$ 2015
Introduction

H\(_+\) PES's

\(\text{H}_2 + \text{H}_3^+\) exchange reaction

\(\text{H}_2 + \text{H}_2^+\) direct reaction

Conclusions

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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 \(\text{H}_2\)
- act as shield for other molecules
- \(\text{M}^+ + \text{H}_2 \rightarrow \text{MH}^+ + \text{H}\)
- \(\text{M} + \text{H}_3^+ \rightarrow \text{MH}^+ + \text{H}_2\)

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 H$_2$ with atoms and ions
  \[ H_2(v = 0) + O^+ \rightarrow OH^+(v', j') + H \]

- Chemistry of H$_2(v > 0)$ in ISM

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

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

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

- Chemistry of 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)

- 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:
    \[ H_3^+ + O \rightarrow H_2 + OH^+ \]
    \[ H_3^+ + O_2 \rightarrow H_2 + O_2H^+ \]
Chemical pumping in molecular clouds and PDR’s

- Exothermic reactions of H₂ with atoms and ions
  \[ H_2(v = 0) + O^+ \rightarrow OH^+(v', j') + H \]

- Chemistry of H₂(\(v > 0\)) 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)

- The most abundant ion is H₃⁺
  - at low T molecules freeze
  - H₃⁺ “lives” longer time
  - H₃ Deuteration occurs
  - Key process for high D/H

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Previous studies on $\text{H}_4^+$.

- **Experimental**
  \[ \text{H}_2^+\text{H}_2^+ (v = 0 - 3) \rightarrow \text{H}_3^+ + \text{H} \text{ and isotopic variants} \]
  Koyano & Tanaka ('80); Anderson *et al.* ('81), Krenos *et al.*('76), ...
  \[ \text{H}_3^+ \text{ infrared spectra, produced in the previous reaction} \]
  Carrington & Kennedy ('84); ...

- **Simulation of the potential**
  Diatomics-in-Molecules potential Muckerman *et al.* ('81)
  PES with frozen $\text{H}_3^+$ Alvarez-Collado *et al.* ('94)
  Interpolated PES in the H+$\text{H}_3^+$ channel Moyano *et al.* ('04)
  Stationary points and intersections along the MEP Varandas ('08)
  No accurate global PES available

- $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ collision simulations
  Quasi-Classical trajectories, with Surface hopping using DIM
  Stine & Muckerman (1976,...) ; Tully & coworkers (1976,...) ; Schatz & coworkers (1985,...) ; ...
H₂ + H₃⁺ exchange collision: ortho/para conversion

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

- Full dimensional PES for $\text{H}_4^+$ and $\text{H}_5^+$
  
  with good long range behavior
  with analytical derivatives and non-adiabatic couplings

- $\text{H}_2^+ + \text{H}_3^+ \rightarrow \text{H}_3^+ + \text{H}_2$ Is the reaction statistical?:

  Going beyond pure statistical approach
  - Introduction of dynamical bias
  - Use global PES

  Comparison with experimental $K^{\text{Hop}}/K^{\text{Exchange}}$

- $\text{H}_2^+ + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$

  Non adiabatic couplings and Conical intersections
  Non adiabatic dynamics: MD with Quantum Jumps
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1. Introduction
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**H⁺: 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


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  
  Aguado *et al* (2000)

- **$H_4^+$ & $H_5^+$**: $V = H_{TRIM} + V_{NB}$

  \[ \hat{H}_{TRIM}(i) = \sum_{n>i,o>n} \hat{H}_{ino}(n-i,o-i) - 2 \sum_{p>i} \hat{H}_{ip}(p-i) \]  
  Sanz *et al.* (2013), Aguado et al.(’10),

- 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. \[ \frac{\partial}{\partial \alpha} (H \phi_n) = \frac{\partial}{\partial \alpha} (W_n \phi_n) \]
and premultiplying by \( \phi_n' \) and integrating

\[
\left< \phi_n' \left| \frac{\partial H}{\partial \alpha} \right| \phi_n \right> = \delta_{nn'} \frac{\partial W_n}{\partial \alpha} + (1 - \delta_{nn'}) (W_n - W_n') \left< \phi_n' \left| \frac{\partial \phi_n}{\partial \alpha} \right> \right]
\]

\[ \phi_n = \sum_d T^d_n f_d \quad \rightarrow \quad \left< \phi_n' \left| \frac{\partial \phi_n}{\partial \alpha} \right> \right> = \sum_{dd'} \frac{(T_{n'}^{d'})^\dagger T^n_d}{W_n - W_n'} \frac{\partial \langle f_{d'} | H | f_d \rangle}{\partial \alpha} \]

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

Analytical: potential derivatives
non-adiabatic matrix elements
for \( \text{H}_3^+, \text{H}_4^+ & \text{H}_5^+ \)
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Production of $H_2D^+$

Ortho/para conversion of $H_3^+$

Large Zero Point energy

$$(HHH)^+ + HH \rightarrow (HHH)^+ + HH$$

inelastic

$$\rightarrow HH + (HHH)^+$$

hop : 3 channels

$$\rightarrow HH + (HHH)^+$$

exchange : 6 channels

Each pathway obeys strict nuclear spin selection rules

This allows to “infer” the hop/exchange ratio: $\alpha = k_H^E / k_E$

Cordonnier et al. (’00)

Crabtree et al. (’11)
H$_3^+$ + H$_2$ → H$_2$ + H$_3^+$ exchange reaction

Each pathway obeys strict nuclear spin selection rules

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

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

$\alpha$ 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:

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

Need of dynamics to describe transition

Parker & Light ('07), Hugo et al. ('09)
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
H₂⁺ H₃⁺: Statistical model of Park & Light, JCP ('07)

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

$$P_{sr,M's'r'}^{JJO}(E) = \frac{gIs \gamma_{sIs'}^{M'} W_{sr\nu\nu^t}^{JJO}(E) W_{sr'd'^t}(E)}{\sum'' \gamma_{sIs''}^{M''} W_{s''r''\nu''t}^{JJO}(E)}$$

1. Nuclear spin statistical weight matrix, $g$
2. Capture probability, $W_{sr\nu\nu^t}^{JJO}$
3. Spin branching ratio matrices, $\gamma_{sIs'}^{M'}$
4. Scrambling matrix, $S_M = \{1/10, 3/10, 6/10\}$

$$(HHH)^+ + HH \rightarrow (HHH)^+ + HH$$

inelastic

$$\rightarrow HH + (HHH)^+$$

hop: 3 channels

$$\rightarrow HH + (HHH)^+$$

exchange: 6 channels

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\( \text{H}_2^+ + \text{H}_3^+ : \text{Statistical model of Park & Light, JCP (’07)} \)

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

\[
P_{sr,M's'r'}^{JI\Omega}(E) = \frac{g_{Is} \gamma_{s'I's}^{M'} W_{sr\nu\Omega_t}^{J\Omega}(E) W_{s'r'\nu'\Omega_t}^{J\Omega}(E)}{\sum'' \gamma_{s'I's''}^{M''} W_{s''r''\nu''\Omega_t}^{J\Omega}(E)}
\]

1. Nuclear spin statistical weight matrix, \( g \)
2. Capture probability, \( W_{sr\nu\Omega_t}^{J\Omega} \)
3. Spin branching ratio matrices, \( \gamma_{s'I's}^{M'} \)
4. Scrambling matrix, \( S_M \) from dynamical calculations

\[ (\text{HHH})^+ + \text{HH} \rightarrow (\text{HHH})^+ + \text{HH} \]
\[ \text{inelastic} \]
\[ \rightarrow \text{HH} + (\text{HHH})^+ \]
\[ \text{hop} : \ 3 \text{ channels} \]
\[ \rightarrow \text{HH} + (\text{HHH})^+ \]
\[ \text{exchange} : \ 6 \text{ channels} \]
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)
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 $\text{H}_2^+ + \text{H}_2^+ \rightarrow \text{H} + \text{H}_3^+$ 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 \}

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

Total reaction cross section using QCT

\begin{align*}
\text{Integral cross section (A}^2\text{)} & \quad \text{Collision energy (eV)} \\
\text{H}_2 + \text{H}_2^+ & \quad A + BCD^+ \\
\text{atom hop} & \quad B + ACD^+ \\
\text{proton hop} & \quad ABC^+ + D \\
\text{exchange} & \quad ABD^+ + C \\
\text{identity} & \quad AC + BD^+ \\
\text{exchange} & \quad AC^+ + BD \\
\end{align*}

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Comparison with experiments

$H_2^+ PES's$

$H_2 + H_3^+ exchange reaction$

$H_2 + H_2^+$ direct reaction

Conclusions

Comparison with experiments

$H_2 + H_2^+ -> H_3^+ + H$

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

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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$_2$D$^+$) > $\rho$(H$_3^+$)

Quantum effects?

- Nuclear spin and symmetry effects?
Non-adiabatic vs charge transfer processes

Crossings: when hydrogen atoms are at equivalent positions

Sanz-Sanz et al. JCP ('13)
Stein & Muckerman, JCP, 68 ('78)
Non-adiabatic couplings & Conical intersections

Energy (eV)

NACME (a.u.)

$r_1$ (a.u.)
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:

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

\[ H_2(v=0) + H_2^+ (v=2), E_c = 1 \text{ eV} \]

\[ \rightarrow H_2^+ + H_2 : \text{exchange} \]

\[ H_2(v=0) + H_2^+ (v=2), E_c = 1 \text{ eV} \]

\[ \rightarrow H_3^+ + H : \text{reactive} \]
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 \( \frac{\partial a_i(t)}{\partial t} \)

- Classical trajectory on \( |1\rangle \) or \( |2\rangle \)
  Energy change along \( \nabla_{ij} \)

Example \( v=0 \) and 2 for \( E_c=0.1 \text{ eV} \)
Surface hopping method (Tully)

**Is adiabatic approach good?**
Initial vibration effect

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

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

Integral cross section (Å\(^2\))
Collision energy (eV)

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Initial vibration effect

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

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Integral Cross Section (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td>Triangles: Experiments at 0.11 eV by Koyano &amp; Tanaka, JCP('80)</td>
</tr>
<tr>
<td>0.5</td>
<td>Open circles: QCT</td>
</tr>
<tr>
<td>1</td>
<td>Full circles: Surface hopping with 2 states</td>
</tr>
</tbody>
</table>

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Collision energy effect

No. electronic transition/trajectory vs. Collision energy (eV)

- \( v = 0 \)
- \( v = 1 \)
- \( v = 2 \)

\[ \text{H}_2 \text{H}_e + \text{H}_2^+ \text{r}_{34} \]

\[ \text{H}_2 \text{r}_{12} + \text{H}_2^+ \text{r}_e \]

E / eV vs. \( r_{12} \) or \( r_{34} \) (Angs.)

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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 $E_{col} < 1$ 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
Collaborators

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

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