Resonant electron-molecular cation collisions in the edge plasmas of fusion devices: new state-to-state cross sections and rate coefficients

J. Zsolt Mezei

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Introduction: Elementary processes

Dissociative recombination
Introduction: Elementary processes

Vibrational excitation
Introduction: Elementary processes

Dissociative excitation
Introduction: Elementary processes

- **AB⁺(v')⁺e⁻**: \( v' < v \) (Ro-)vibrational de-excitation, SUPERelastic collision
- **AB⁺(v)⁺e⁻**: Elastic collision
- **AB⁺(v')⁺e⁻**: \( v' > v \) (Ro-)vibrational excitation, INelastic collision

Electron/cation reactions

- **A(n)⁺ⁿ⁺**: Dissociative recombination
- **A⁺⁺⁺**: Dissociative excitation
- **A⁺⁺⁺**: Dissociative excitation
- **A⁺⁺⁺**: Dissociative excitation
- **A⁺⁺⁺**: Dissociative excitation

**AB, AB⁺, AB⁺⁺**
Introduction: Elementary processes

Photoabsorption: $h\nu + AB$

Photoionization: $AB^+(v) + e^-$

Photodissociation: $A^+ + B + e^-$

Photofragmentation: $AB, AB^*, AB^{**}$

Dissociative photoionization: $A(n) + B(n^*)$
Introduction: Elementary processes

- **Associated ionization**: $AB^+ (v) + e^-$
- **Anion/cation reactions**: $A^+ + B^-$
- **Mutual neutralization**: $A(n) + B(n^*)$
- **Charge transfer**: $A^- + B^+$
- **$AB, AB^*, AB^{**}$**
Introduction: Elementary processes

- Photoionization: \( AB^+(v') + e^- \rightarrow AB(v) + e^- \)
  - (Ro-)vibrational de-excitation, SUPERelastic collision
- Elastic collision: \( AB \rightarrow AB \) \( \rightarrow AB, AB^*, AB^{**} \)
- Electron/cation reactions: \( AB^+(v') + e^- \rightarrow AB(v') + e^- \)
- Associative ionization: \( AB + e^- \rightarrow A^+ + B^- \)
- Anion/cation reactions: \( A^+ + B^- \rightarrow AB \)
- Dissociative recombination: \( A(n) + B(n') \rightarrow AB \)
- Dissociative excitation: \( h\nu + AB \rightarrow AB \)
- Mutual neutralization: \( A(n) + B(n') \rightarrow A + B \)
- Photodissociation: \( A + B + e^- \)
- Photodissociation: \( h\nu + AB \rightarrow AB \)
Introduction: Cold ionized media

- Interstellar molecular clouds
- Planetary atmospheres
- Cold laboratory plasmas
- At the wall of the fusion devices (ITER) project

- Hypersonic entry of spacecrafts
- Plasma-assisted depollution
- Electric-field-assisted combustion
- Plasma-assisted combustion
Theoretical approach: Reactive collisions

$$e^- + AB^+(v_i^+, N_i^+) \rightarrow AB^*, AB^{**} \rightarrow \begin{cases} AB^+(v_f^+, N_f^+) + e^- \quad \text{EC, IC, SEC} \\ [A + B]_\epsilon \quad \text{DR} \\ A^+ + B + e^- \quad \text{DE} \end{cases}$$

Poster of J. Zs. Mezei et al
Theoretical approach: MQDT

Multichannel Quantum Defect Theory

Seaton (1958-1983), Fano, Jungen, Greene, Giusti-Suzor (1970-...), ...

Quantum Interferences

DIRECT

Dissociative state

\[ e^- + AB^+ \rightarrow AB^{**} \rightarrow A^+ + B \]

BOUND (Rydberg) state

INDIRECT

CHANNEL interactions

Dissociative excitation

Ionisation

Zone de réaction \( AB^*, AB^{**} \)

Dissociation

\[ R(A - B) \]
MQDT: DR mechanisms

\[ H_2^+ + e^- \Rightarrow H(n) + H(n') + \text{KER} \]

Direct process

Indirect process

Kinetic Energy Release

Rydberg state

Interference

H(1s) + H(2I)
Case study: \( \text{SH}^+ \)

**Discovery:** Benz *et al* (2010)

**Formation and destruction routes**

\[ \text{S}^+ + \text{H}_2 \rightarrow \text{SH}^+ + \text{H} \ (-0.86 \text{ eV}) \]

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**A theoretical study of the dissociative recombination of \( \text{SH}^+ \) with electrons through the \( ^2\Pi \) states of \( \text{SH} \)**

D. O. Kashinski, D. Talbi, A. P. Hickman, O. E. Di Nallo, F. Colboc, K. Chakrabarti, F. Schneider, and J. Zs. Mezei

1. Department of Physics and Nuclear Engineering, United States Military Academy, West Point, New York 10996, USA
2. Laboratoire Univers et Particules de Montpellier, Université de Montpellier, CNRS, Place Eugène Bataillon, 34095 Montpellier, France
3. Department of Physics, Lehigh University, 16 Memorial Drive East, Bethlehem, Pennsylvania 18015, USA
4. Laboratoire Ondes et Milieux Complexes, UMR 6294, Université Le Havre, 25, Rue Philippe Lebon, BP 540, F-76658 Le Havre, France
5. Department of Mathematics, Scottish Church College, 1 and 3 Urquhart Square, Calcutta 700 006, India
6. Laboratoire Aimé Cotton UMR 9188 CNRS, University Paris-Sud/ENS Cachan, Bâtiment 505, Campus d’Orsay, 91405 Orsay Cedex, France
7. Laboratoire des Sciences des Procédés et des Matériaux, UPR 3407, Université Paris 13, 95 Avenue Jean-Baptiste Clément, F-93450 Villetaneuse, France

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A quantitative theoretical study of the dissociative recombination of \( \text{SH}^+ \) with electrons has been carried out. Multireference, configuration interaction calculations were used to determine accurate potential energy curves for \( \text{SH}^+ \) and \( \text{SH} \). The block diagonalization method was used to disentangle strongly interacting \( \text{SH} \) valence and Rydberg states and to construct a diabatic Hamiltonian whose diagonal matrix elements provide the diabatic potential energy curves. The off-diagonal elements are related to the electronic valence-Rydberg couplings. Cross sections and rate coefficients for the dissociative recombination reaction were calculated with a stepwise version of the multichannel quantum defect theory, using the molecular data provided by the block diagonalization method. The calculated rates are compared with the most recent measurements performed on the ion Test Storage Ring (TSR) in Heidelberg, Germany. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4983690]

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**Abstract**

**Context:** Tens of light hydrides and small molecules have now been detected over several hundreds sightlines sampling the diffuse interstellar medium (ISM) in both the Solar neighbourhood and the inner Galactic disk.

**Aims:** These new data confirm the limitations of the traditional chemical pathways driven by the UV photons and the cosmic rays (CR) and the need for additional energy sources, such as turbulent dissipation, to open highly endothermic formation routes. The goal of the present paper is to further investigate the link between specific species and the properties of the turbulent cascade in particular its space-time intermittency.

**Methods:** We have analyzed ten different atomic and molecular species in the framework of the updated model of turbulent dissipation regions (TDR). We study the influence on the abundances of these species of parameters specific to chemistry (density, UV field, and CR ionization rate) and those linked to turbulence (the average turbulent dissipation rate, the dissipation timescale, and the ion-neutral velocity drift in the regions of dissipation).

**Results:** The most sensitive tracers of turbulent dissipation are the abundances of \( \text{CH}^+ \) and \( \text{SH}^+ \), and the column densities of the \( J = 3, 4, 5 \) rotational levels of \( \text{H}_2 \). The abundances of \( \text{CO}, \text{HCN}^+ \), and the intensity of the 158 µm [CH] emission line are significantly...
MQDT: molecular data

![Graphical representation of molecular data]

**SH**

**SH**$^+$

**SH**$^*$

**SH**$^{**}$

**SH**$^{**}$

SH$^+\Delta$

C$_2$: S$^{(2}\Delta)+H(1s)$

C$_1$: S$^{(4}\Sigma)+H(1s)$

D$_1$: S$^{(1}\Pi)+H(1s)$

D$_2$: S$^{(3}\Pi)+H(1s)$

SH$^++H(1s)$

$
\begin{align*}
\text{Coulomb} (\text{a.u}) & \\
\text{Energy} (\text{a.u}) & \\
\text{Quantum defect} & \\
\text{GAMESS + Block diagonalization method (Kashinksi, Hickman, Talbi)}
\end{align*}$
MQDT: The formalism
MQDT: The formalism

\[ \kappa = \nu + \nu \frac{1}{E - H_0} \nu, \]

Lippman-Schwinger equation
MQDT: The formalism

The reaction zone
K-matrix -> eigenchannels

3.
\[ \kappa U = -\frac{1}{\pi} \tan(\eta) U , \]
MQDT: The formalism

The reaction zone

Frame Transformation

4. Asymptotic region

\[
C_{\nu c^+ \Lambda \alpha} = \sum_{\nu c^+} U_{\nu c^+, \alpha} \left\langle \chi_{\nu c^+} (R) \right| \cos \left( \pi \mu_{c^+} (R) + \eta_{\alpha} \right) \left| \chi_{\nu c^+} (R) \right\rangle
\]

\[
C_{d \lambda \alpha} = U_{d \lambda, \alpha} \cos \eta_{\alpha}
\]

\[
S_{\nu c^+ \Lambda \alpha} = \sum_{\nu c^+} U_{\nu c^+, \alpha} \left\langle \chi_{\nu c^+} (R) \right| \sin \left( \pi \mu_{c^+} (R) + \eta_{\alpha} \right) \left| \chi_{\nu c^+} (R) \right\rangle
\]

\[
S_{d \lambda \alpha} = U_{d \lambda, \alpha} \sin \eta_{\alpha}
\]
MQDT: The formalism

\[ \chi = \frac{C + iS}{C - iS} \]

Cayley Transformation

- \( \chi \) : open channels
- \( \chi \) : closed channels

5. \( \chi \) : open channels

\[ \begin{pmatrix} X_{oo} & X_{oc} \\ X_{co} & X_{cc} \end{pmatrix} \]
MQDT: The formalism

The scattering matrix:

\[ S = X_{oo} - X_{oc} \frac{1}{X_{cc} - \exp(-i2\pi\nu)} X_{co}. \]
MQDT: The formalism

\[ \sigma_{\text{diss} \leftarrow v_i^+} = \sum_{\Lambda} \frac{\pi}{4\varepsilon} \rho^\Lambda \sum_{j} | S_{d_j, v_i^+} |^2, \]

The DR cross section
**SH⁺: DR xs**

- **Direct process**

- DR cross section (cm²)

- **C₁ - D₁**

- Energy (a.u)

- R (Å)

- Coupling (a.u)
**SH⁺: DR xs**

**direct process**

![Graph showing DR cross sections and energy variations.](image)
SH\(^+\): DR xs

direct process

\[ \text{DR cross section (cm}^2) \]

\[ C_1 \& C_2 - D_1 \]

\[ C_1 - D_1 \]
**SH^+: DR xs**

**direct process**

**Graph:**
- **x-axis (E, eV):** 0.01, 0.1, 1
- **y-axis (DR cross section, cm^2):** 10^{-13}, 10^{-14}, 10^{-15}, 10^{-16}, 10^{-17}, 10^{-18}

**Lines:**
- **C_1 - D_1**
- **C_1& C_2 - D_1 & D_2**
- **C_2 - D_2**

**Plot:**
- **Energy (a.u.):** -399.8 to -399.2
- **R (Å):** 0 to 8

**Legend:**
- **SH^+ 1Δ**
- **C_2: S*(D)+H(1s)**
- **SH^+ 3Σ^−**
- **C_1: S*(S)+H(1s)**
- **SH^+ 2Σ**
- **D_1: S(D)+H(1s)**
- **D_2: S(P)+H(1s)**

**Equations:**
- **C_1:** S + (4So) + H(1s)
- **D_2:** S(3P) + H(1s)
- **C_2:** S + (2D) + H(1s)
- **SH + 1 Δ:** × 0.5
**SH⁺: DR xs**

*direct process*

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

- **DR cross section (cm²)** vs. **E (eV)**
  - **C₁ & C₂ - D₁ & D₂**
  - **C₁ & C₂ - D₁**
  - **C₁ - D₁ & D₂**
  - **C₁ - D₁**

**Energy (a.u)**
- **C₁**: S⁺(D) + H(1s)
- **D₂**: S(1D) + H(1s)
- **C₂**: S⁺(S) + H(1s)
- **D₁**: S(1S) + H(1s)

![Graph showing coupling vs. R (Å)](image)

- **R (Å)**
  - 0.01, 0.02, 0.03, 0.04, 0.05, 0.06

![Graph showing R (Å) vs. Energy (a.u)](image)
**SH**: DR xs

![Graph showing DR cross section vs. energy and R (Å).](image)

- **Total process**
- **DR cross section (cm²)**
- **Energy (a.u)**
- **Quantum defect**

**Equations**:

\[ \text{SH}^+ : \text{DR xs} \]

\[ \text{C}_1 - \text{D}_1 \]

\[ \text{SH}^{+ \, 2\Sigma} - \text{D}_1 : \text{S}(^1\text{D}) + \text{H}(1s) \]

\[ \text{SH}^{+ \, 2\Pi} - \text{C}_1 : \text{S}(^4\text{S}) + \text{H}(1s) \]
SH\(^{+}\): DR xs

total process

E (eV)

10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
10^{-18}

0.01
0.1
1

E (eV)

R (Å)

1
2
3
4
5
6
7
8

quantum defect

0.2
0.4
0.6
0.8

R (Å)

0.2
0.4
0.6
0.8

counting (au^{1/2})
**SH⁺: DR xs**

![Graph showing DR cross section vs. energy and internuclear distance for different processes.](image)

- **Total process**
- **DR cross section (cm²) vs. energy (eV)**
- **Energy (a.u.) vs. internuclear distance (Å)**

**Quantum defect**

- **C₁ & C₂ - D₁**
- **C₁ - D₁**

**Processes:**
- SH⁺ 1Δ
- C₂: S⁺(1D) + H(1s)
- SH⁺ 3Σ⁺
- C₁: S⁺(3P) + H(1s)
- SH⁺ 2Π
- D₁: S(1D) + H(1s)
**SH**: DR xs

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

**Total process**

- $C_1$: $S^+(1D) + H(1s)$
- $C_2$: $S(3P) + H(1s)$
- $D_1$: $S^+(1D) + H(1s)$
- $D_2$: $S(3P) + H(1s)$

**Quantum defect**

Energy (a.u) vs. R (Å)
$\text{SH}^+: \text{DR rate}$

\[
\alpha(T) = \left( \frac{m_e}{2\pi kT} \right)^{3/2} \int_0^\infty \sigma(v)v \exp \left( -\frac{m_e v^2}{2kT} \right) 4\pi v^2 \, dv
\]

Maxwell isotropic rate coefficient (cm$^3$ s$^{-1}$)

- Blue: $C_1$ & $C_2$ - $D_1$ & $D_2$
- Red: $C_1$ & $C_2$ - $D_1$
- Green: $C_1$ - $D_1$

- Dashed: direct process
- Solid: total process

Temperature (K)
Results: **The most abundant molecule**

$H_2$

Densities $\sim 10^5 - 10^{-7} \text{ cm}^{-3}$

$T \sim 30000 \text{ K} - 0.003 \text{ K}$

Warm ionized medium (densities $\sim 0.3 \text{ cm}^{-3}$ - $T \sim 10000 - 8000 \text{ K}$)

Warm neutral medium (densities $\sim 0.3 \text{ cm}^{-3}$ - $T \sim 8000 \text{ K}$)

Cold neutral medium (densities $\sim 30 \text{ cm}^{-3}$ - $T \sim 50 \text{ K}$)

Molecular clouds (densities $> 100 \text{ cm}^{-3}$ - $T > 10 \text{ K}$)

Some orders of magnitude:

* $n_e = 10^8 - 10^{12} \text{ cm}^{-3}$ ($< 10^{-2}$ and more often $< 10^{-5}$)
* $\langle \varepsilon_c \rangle = 1 - 10 \text{ eV}$
* $T_g = 300 - 6000 \text{ K}$
* $T_v = 1000 - 5000 \text{ K}$ (molecular gases)
Results: The most abundant molecule @ low temperatures

- **Rotational excitation**

ANR: Faure & Tennyson MNRAS (2001)

- **Dissociative recombination**

Reactive collisions of very low-energy electrons with H$_3^+$: rotational transitions and dissociative recombination

M. D. Epée Epée,$^1$ J. Zs Mezei,$^{2,3,4}$ O. Motapon,$^{1,5*}$ N. Pop$^6$ and I. F. Schneider$^{2,3*}$

*and its isotopologues*
Results: The most abundant molecule at medium temperatures

in progress for its isotopologues
Results: The most abundant molecule @ high temperatures

Dissociative Recombination

$\ce{HD}^+ + \ce{e^-} \rightarrow \ce{H} + \ce{D}$

K. Chakrabarti et al, 2013

Cross Section (cm$^2$)

Energy (eV)

Cross Section (cm$^2$)

in progress for its isotopologues
Results: **Molecules in fusion experiments**

- **Wall materials**
  - ITER: Be, W and C
  - ASDEX Upgrade: W
  - ITER like wall of JET: Be, W
  - Boronization of the walls (impurities, recycling)

- **Low temperatures in the plasma edge**
  - $\Rightarrow$ formation of molecules

- **Recycling at the wall**
  - $H_2, D_2, T_2, HD, HT, DT$

- **Plasma wall interaction**
  - $CH, CD, CT, C_2$
  - $BeH, BeD, BeT$
  - $BH, BD, BT$
Results: CH$^+$

Dissociative recombination

State-to-state chemistry and rotational excitation of CH$^+$ in photon-dominated regions

Results: CH⁺

Dissociative recombination of the CH⁺ molecular ion at low energy

K Chakrabarti¹,², J Zs Mezei¹,³,⁴, O Motapon⁵, A Faure⁶, O Dulleu⁷, K Hassouni⁸ and I F Schneider⁹

Poster of N. Pop et al and K. Chakrabarti et al.

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Energy (eV)

DR cross section (cm²)

0.01 0.1

0.01 0.1
Conclusions

• MQDT: state-to-state calculations

• Temporary captures into super-excited states: **HUGE RESONANT EFFECTS**

• Data needs: di- and poly-atomics
In collaboration with

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