# Electron –ion recombination

FP I ZS 2015 -7A

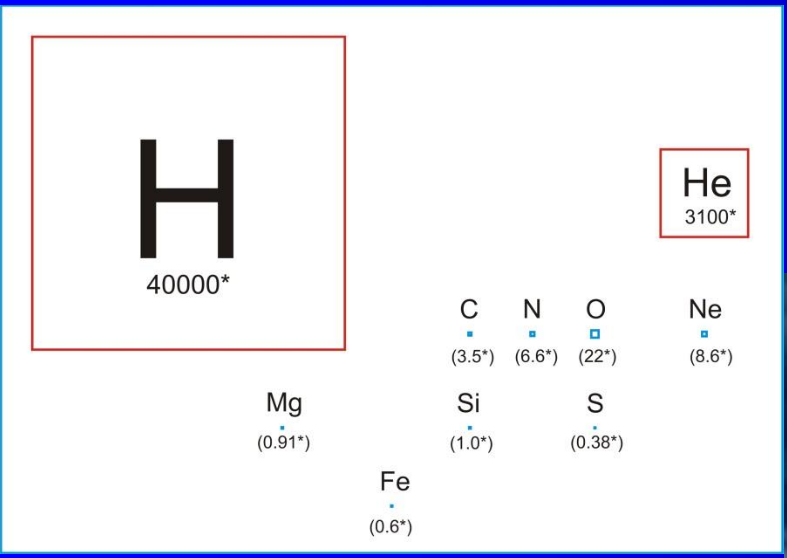
$H^+ + e^- \rightarrow$ products

$H_2^+ + e^- \rightarrow$ products

$H_3^+ + e^- \rightarrow$ products

$H_5^+ + e^- \rightarrow$ products

**92.1% of nucleons in the universe are protons**
**7.8% are helium nuclei !**






Andromeda

# Ion –ion recombination

$H^{+} + C_6H^{-} \rightarrow$ products

$H^{+} + C_8H^{-} \rightarrow$ products

*Note added in manuscript.*—While this Letter was being submitted, $C_8H^-$, the next ion in the series, was detected here—a crucial confirmation of the present identification. Details will be presented elsewhere. An astronomical search is underway.

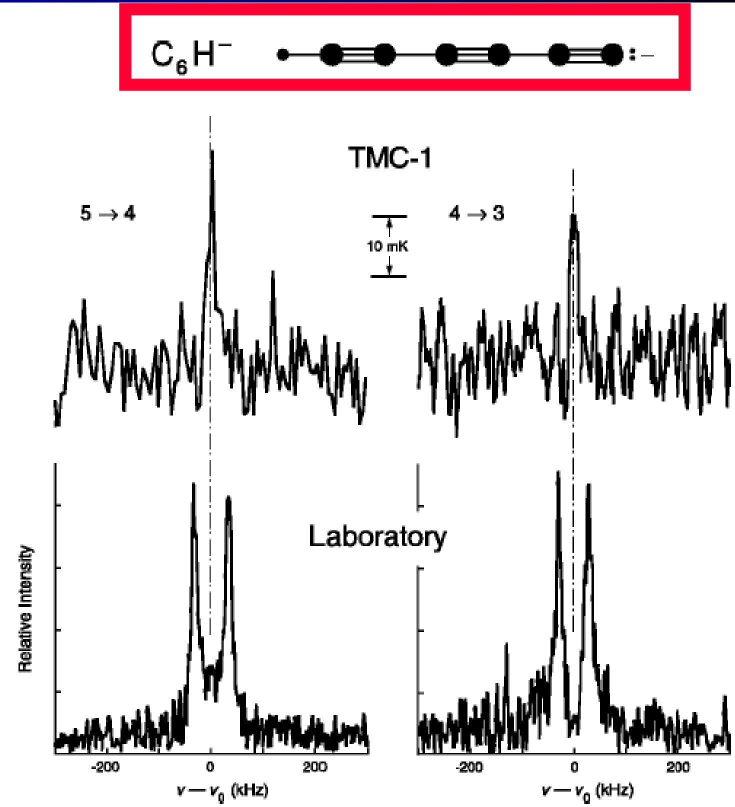



FIG. 1.—Two rotational transitions of $C_6H^-$ in the laboratory and in TMC-1. Frequencies are relative to the laboratory rest frequencies (Table 1), assuming the standard mean radial velocity of 5.80 km $s^{-1}$ for TMC-1. The geometrical structure of $C_6H^-$, the hexatriyne anion, obtained by removing $H^+$ from triace-

THE ASTROPHYSICAL JOURNAL, 652: L141–L144, 2006 December 1


LABORATORY AND ASTRONOMICAL IDENTIFICATION OF THE NEGATIVE MOLECULAR ION $C_6H^-$

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*Received 2006 September 28; accepted 2006 October 17; published 2006 November 20*

ABSTRACT

The negative molecular ion $C_6H^-$ has been detected in the radio band in the laboratory and has been identified in the molecular envelope of IRC +10216 and in the dense molecular cloud TMC-1. The spectroscopic constants derived from laboratory measurements of 17 rotational lines between 8 and 187 GHz are identical to those derived from the astronomical data, establishing unambiguously that $C_6H^-$ is the carrier of the series of lines with rotational constant 1377 MHz first observed by K. Kawaguchi et al. in IRC +10216. The column density of $C_6H^-$ toward both sources is 1%–5% that of neutral $C_6H$. These surprisingly high abundances for a negative ion imply that if other molecular anions are similarly abundant with respect to their neutral counterparts, they may be detectable both in the laboratory at high resolution and in interstellar molecular clouds.

# Recombination processes in plasma

## Binary Recombination

$$H^+ + e \to H + h\nu$$ RR

$$O_2^{\ +} + e \to O + O$$ DR

$$Fe^{7+} + e \to Fe^{6+}$$ DiR

$$\frac{dn_e}{dt} = \frac{d[O_2^{\ +}]}{dt} = -\alpha[O_2^{\ +}]n_e = -\alpha n_e^{\ 2}$$

## Ternary electron assisted recombination

$$Ar^+ + e + e \to Ar + e$$

$$\frac{dn_e}{dt} = \frac{d[Ar^+]}{dt} = -K_e[Ar^+]n_e^{\ 2} = -\alpha_{eff}[Ar^+]n_e$$

**Collisional Radiative Recombination CRR**

$$\alpha_{eff} = K_e n_e$$

## Ternary neutral assisted recombination

$$Ar^+ + e + He \to Ar + He$$

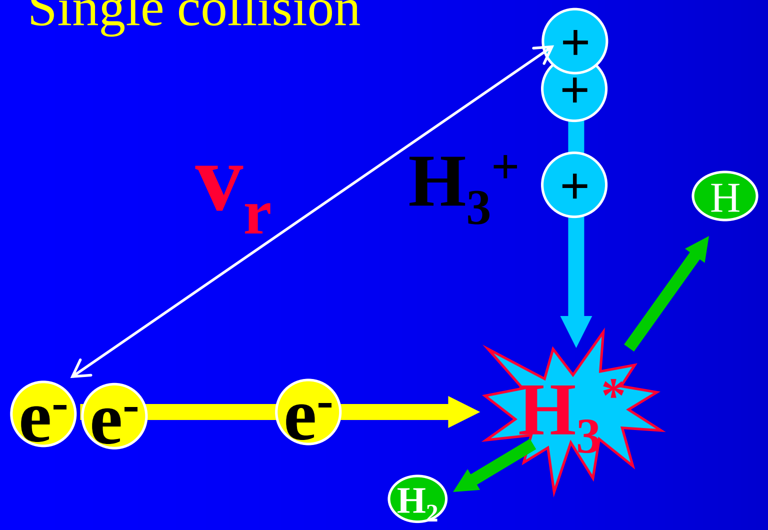
$$\frac{dn_e}{dt} = \frac{d[Ar^+]}{dt} = -K_M[Ar^+]n_e[He] = -\alpha_{eff}[Ar^+]n_e$$

$$\alpha_{eff} = K_M[He]$$

# Cross section

$H_3^+ + e^- \rightarrow H + H_2; 3H$

Single collision



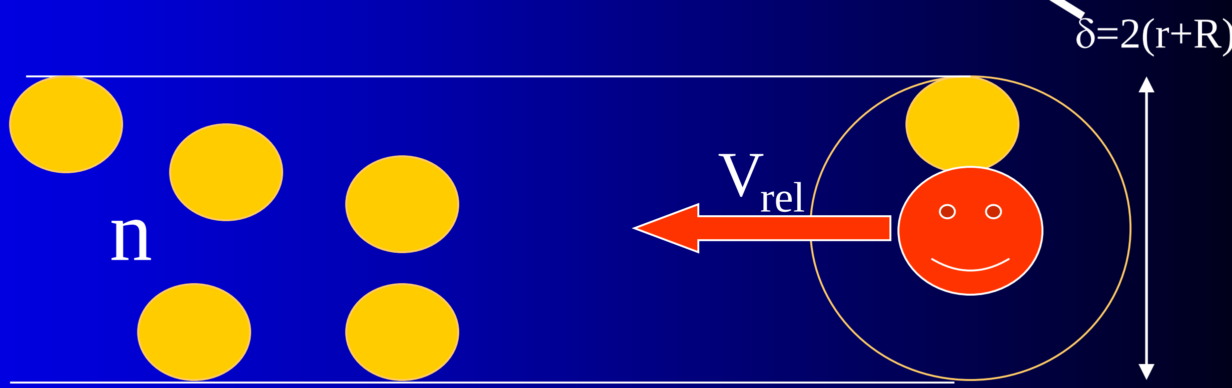

$\sigma(v_r)$

# Electron Neutral interaction

$$\nu_{coll} = nV_{rel} = n v S = n v \pi \delta^2 = n v \sigma$$

$$\nu_{coll} = n v_{rel} \sigma$$

$$\frac{dI}{dt} = -\frac{I}{\tau_{coll}} = -I \nu_{coll}$$




$$I(t) = I_0 \exp(-\nu_{coll} t) = I_0 \exp(-\sigma n v_{rel} t)$$

$I = I_0 \exp(-\sigma n_{Ar} x)$

$H_3^+ + e^- \rightarrow H + H_2; 3H$

Concept of gas phase chemistry

# Recombination in electron – ion plasma

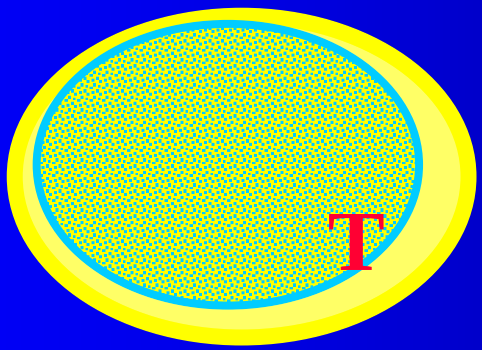
$\alpha(T)$ Rate coefficient

T

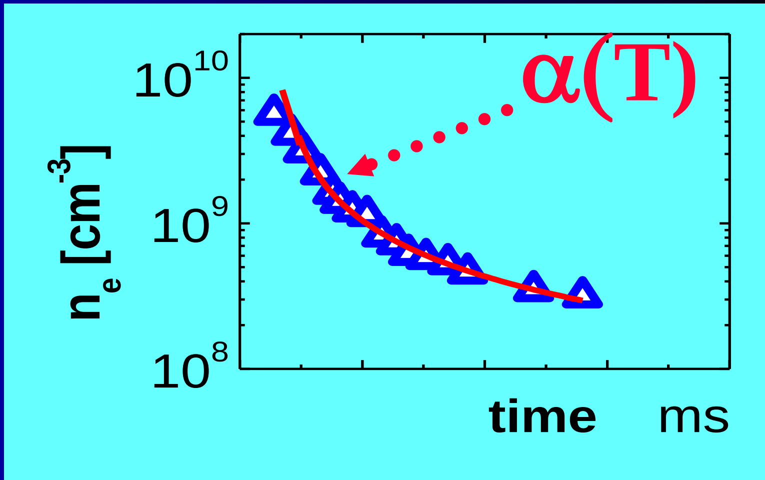
Multiple collisions

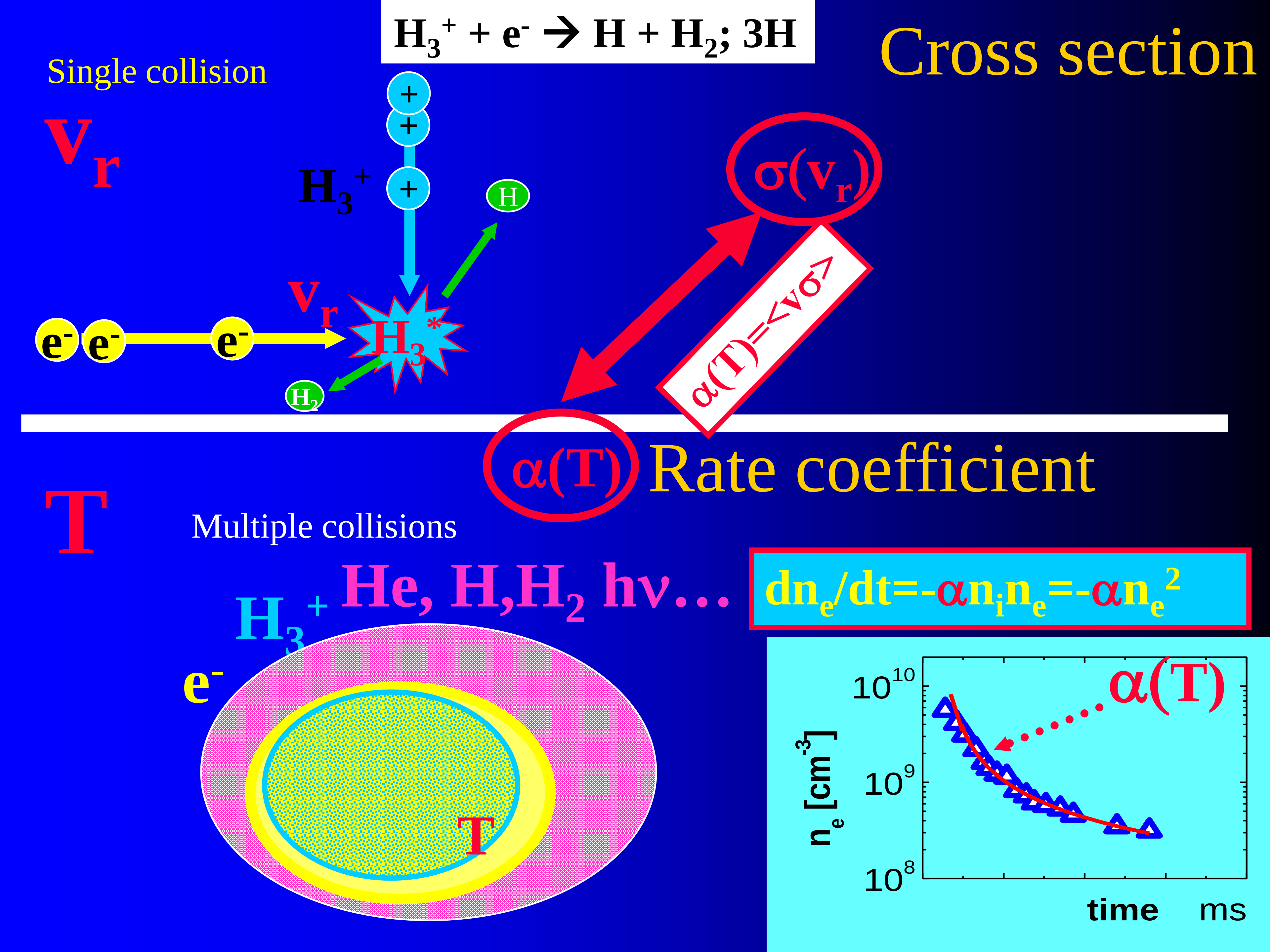
$H_3^+$

$e^-$




$$dn_e/dt = -\alpha n_i n_e = -\alpha n_e^2$$



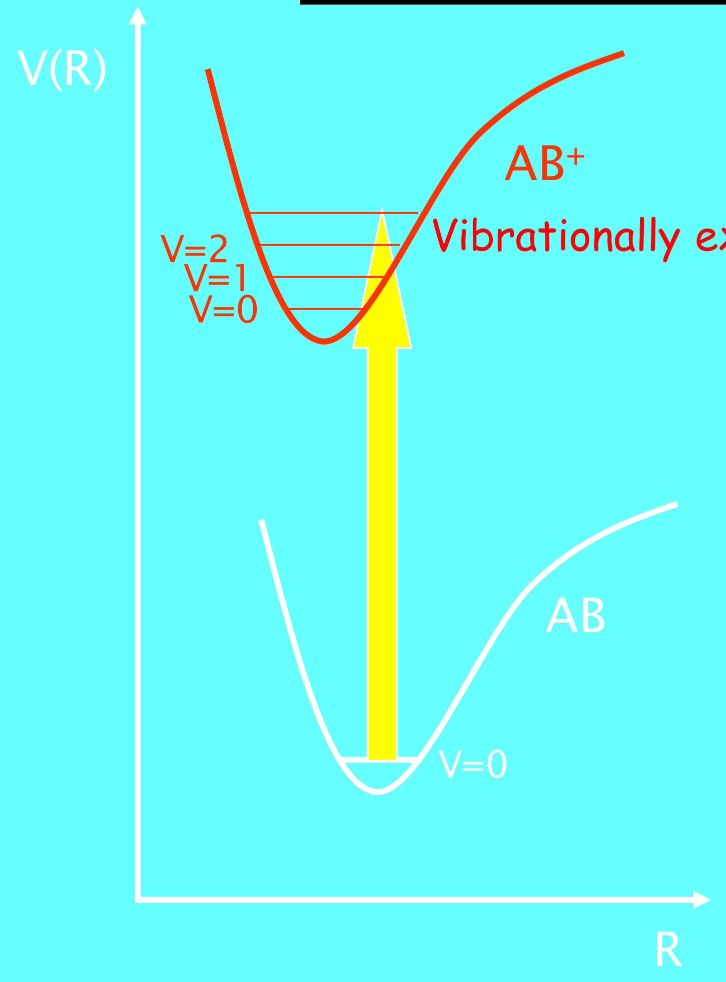


$H_3^+ + e^- \rightarrow H + H_2; 3H$
Cross section
Single collision
$v_r$
$H_3^+$
H
$v_r$
$H_3^*$
$e^-$ $e^-$ $e^-$
$H_2$
$\sigma(v_r)$
$\alpha(T)=\langle v\sigma \rangle$
$\alpha(T)$ Rate coefficient
T
Multiple collisions
He, H,$H_2$ hν…
$dn_e/dt=-\alpha n_i n_e=-\alpha n_e^2$
$H_3^+$
$e^-$
T
$10^{10}$
$10^9$
$10^8$
$n_e$ [$cm^{-3}$]
$\alpha(T)$
time ms

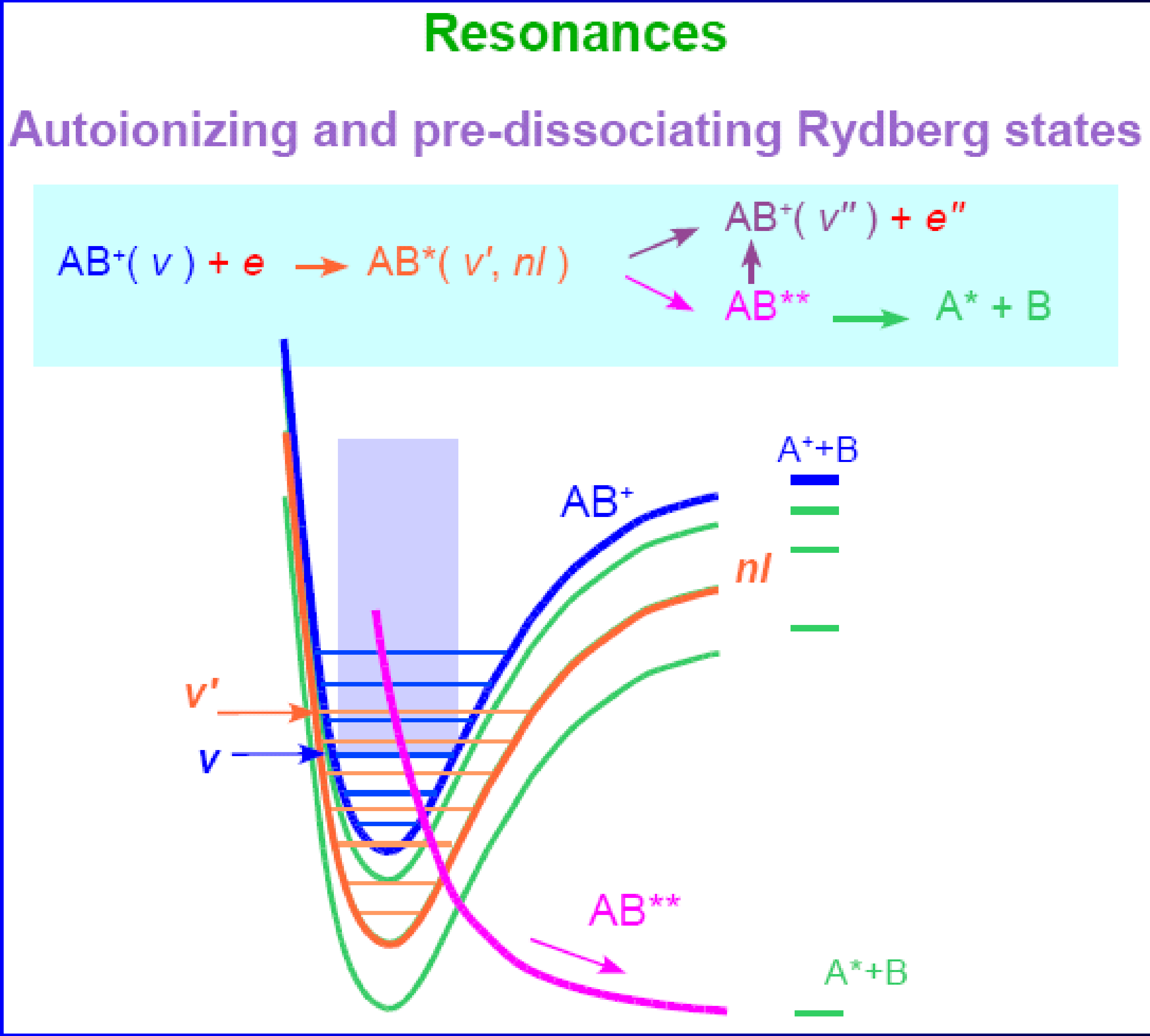
Electron neutral interaction

Born-Oppenheimer

$$P(v) \propto \langle \Psi_{AB}(R) | \Psi_{AB+}(R) \rangle$$



# Resonances



Resonances
Autoionizing and pre-dissociating Rydberg states
AB⁺( v ) + e → AB*( v′, nl )
AB⁺( v″ ) + e″
AB**
A* + B
A⁺+B
AB⁺
nl
v′
v
AB**
A*+B

# Electron - Ion Collision

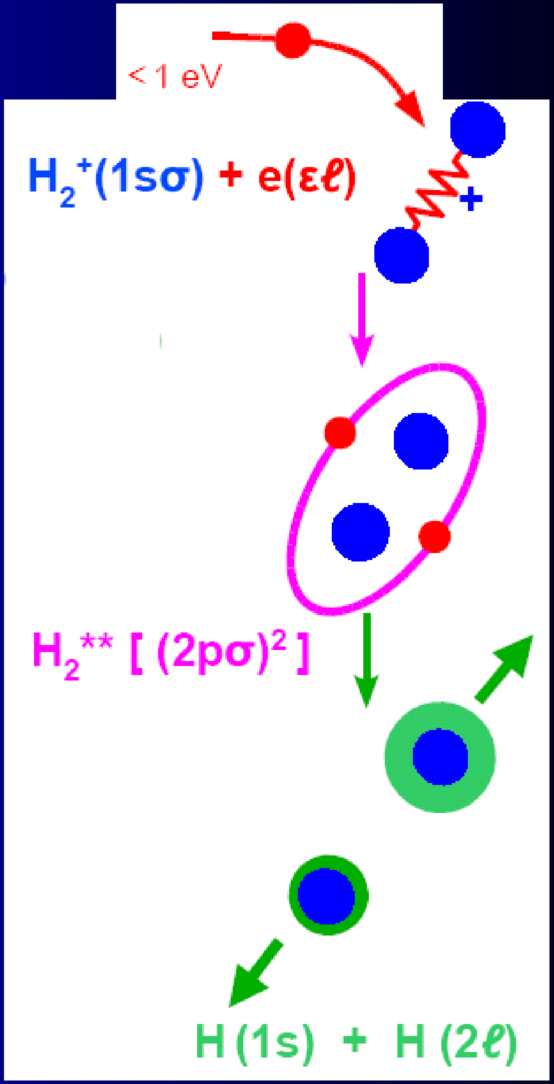
$H^+ + e^- \rightarrow$ ~ no recombination

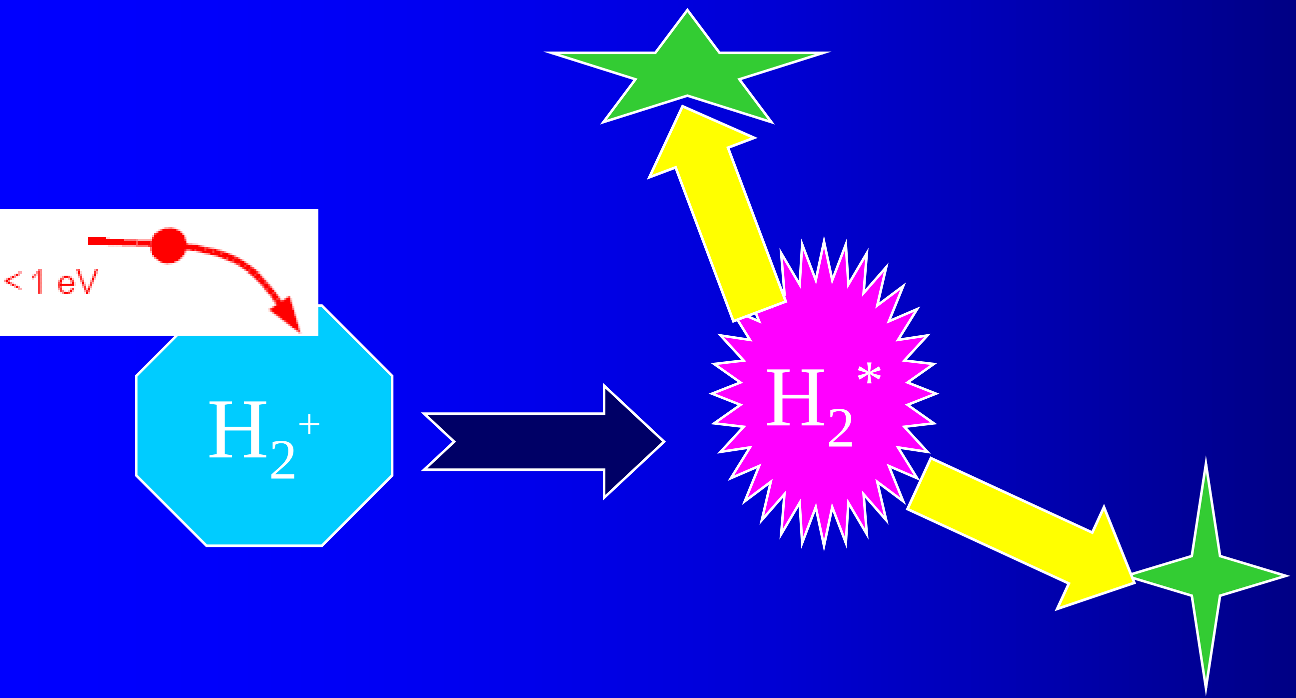
$H^+ + e^- \rightarrow H + h\nu$ RR

$H^+ + e^- + e^- \rightarrow H + e^-$ ternary CRR

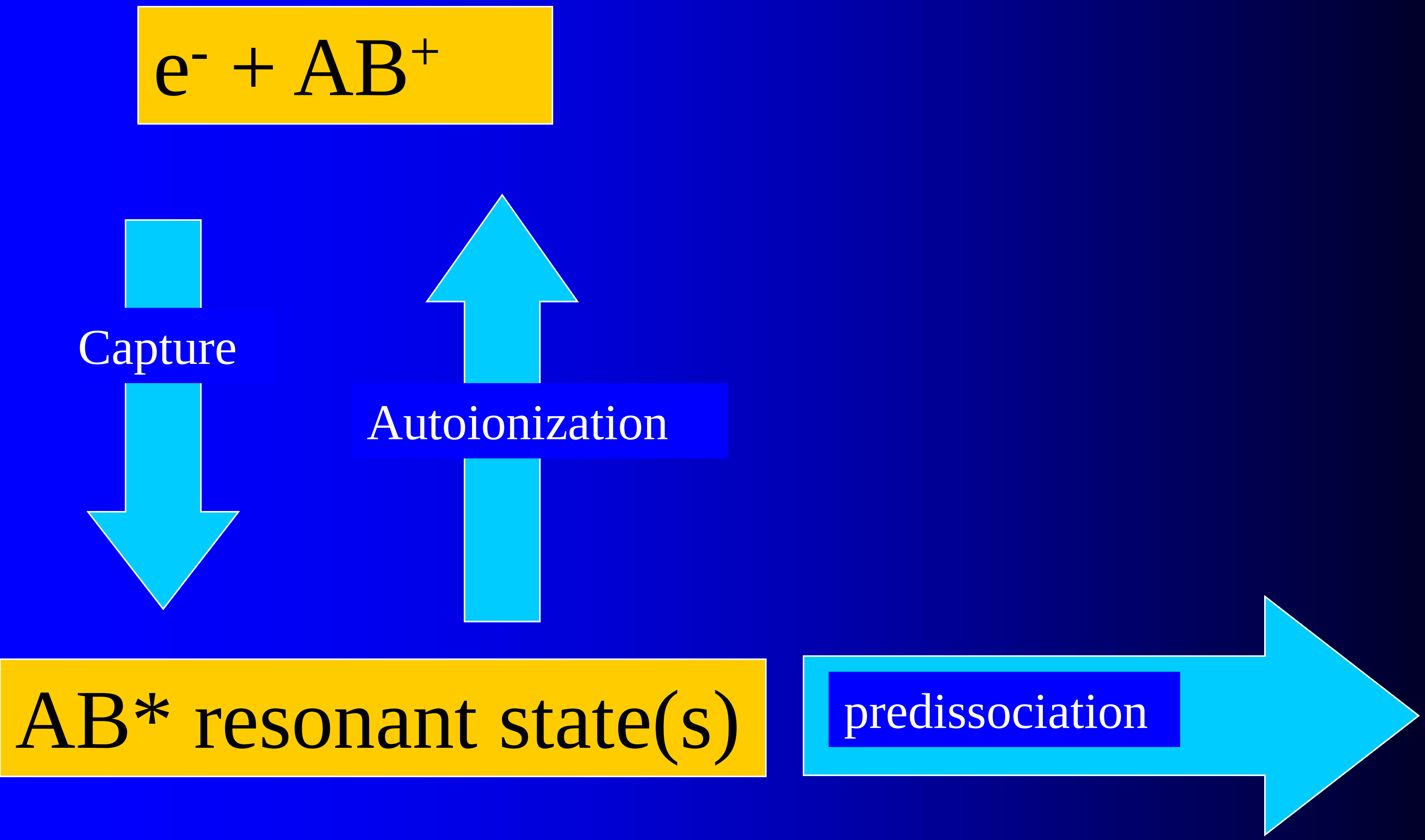
$H_2^+ + e^- \rightarrow$ H + H,

<u>Dissociative Recombination</u> - DR




Electron collisions with $H_2^+$ - how to describe ????



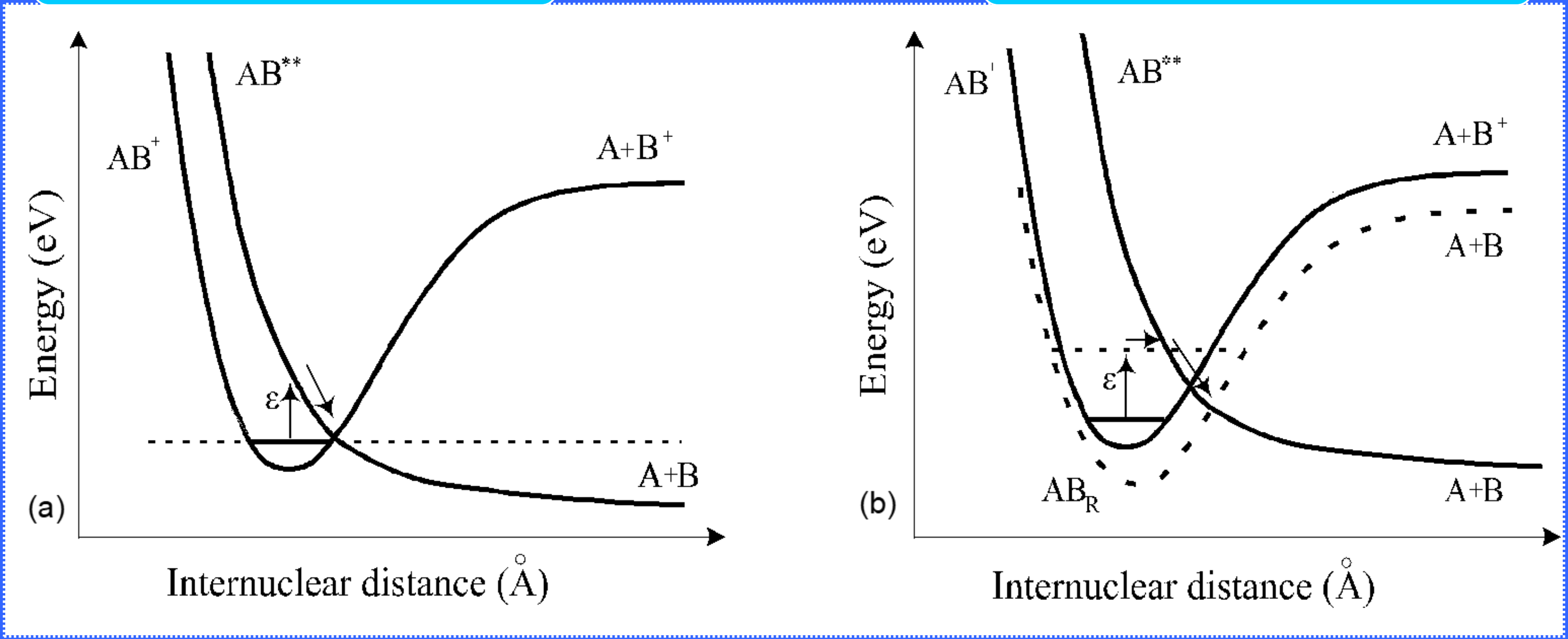

To get high recombination rate, we need

(a) efficient capture

(b) predissociation faster than auto-ionization

# Direct DR process

# Indirect DR process




$$AB^{+} + e^{-} \underset{k_{auto}}{\overset{k_c}{\rightleftarrows}} AB^{**} \xrightarrow{k_{stab}} A + B$$

$$AB^{+} + e^{-} \rightleftarrows AB_R^{**} \rightleftarrows AB^{**} \rightarrow A + B$$

$$\alpha_{dr} \approx T_e^{-0.5}$$

$$\alpha_{idr} \approx T_e^{-1.5}$$

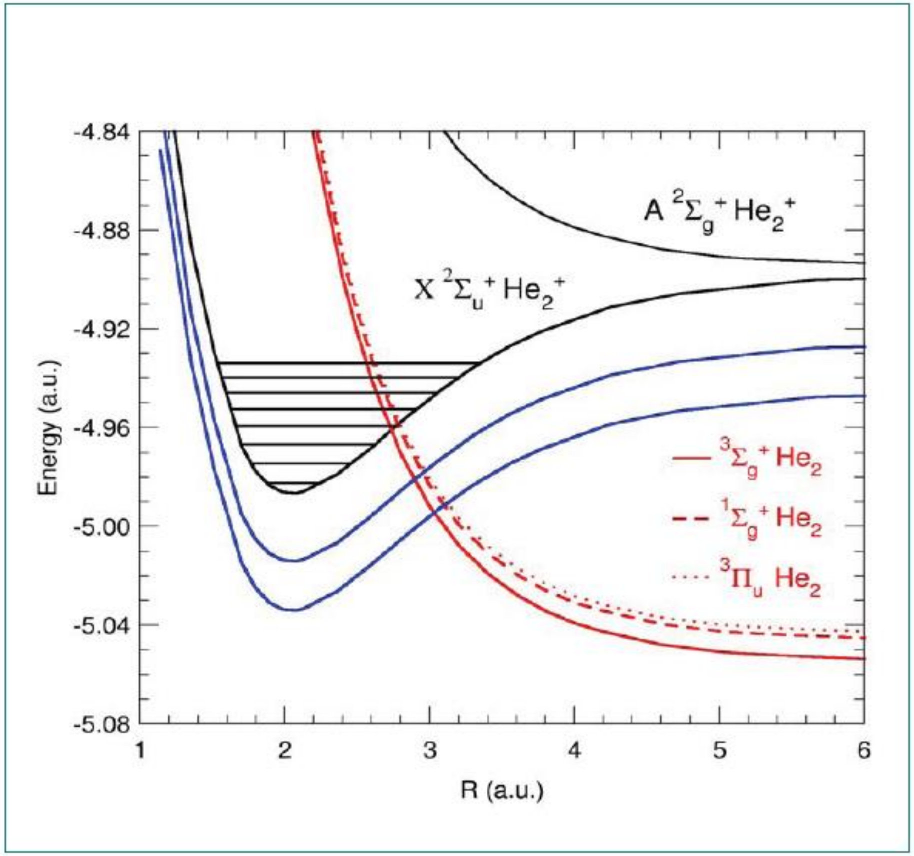
$$\alpha(T_e, T_v) \approx T_e^{-0.5} T_v^{-1}$$

**Ions: $Ar_2^+$, $N_2^+$, $CH_4^+$, $NH_4^+(NH_3)_2$ - $\alpha \sim 10^{-7} – 10^{-6}$ cm$^3$ s$^{-1}$**

**Theoretical calculation: $H_2^+$, $HD^+$, $D_2^+$- $\alpha = 2.3\times10^{-8}$, $2.2\times10^{-8}$, $4\times10^{-9}$ cm$^3$ s$^{-1}$, respectively**

# THEORETICAL FRAMEWORK

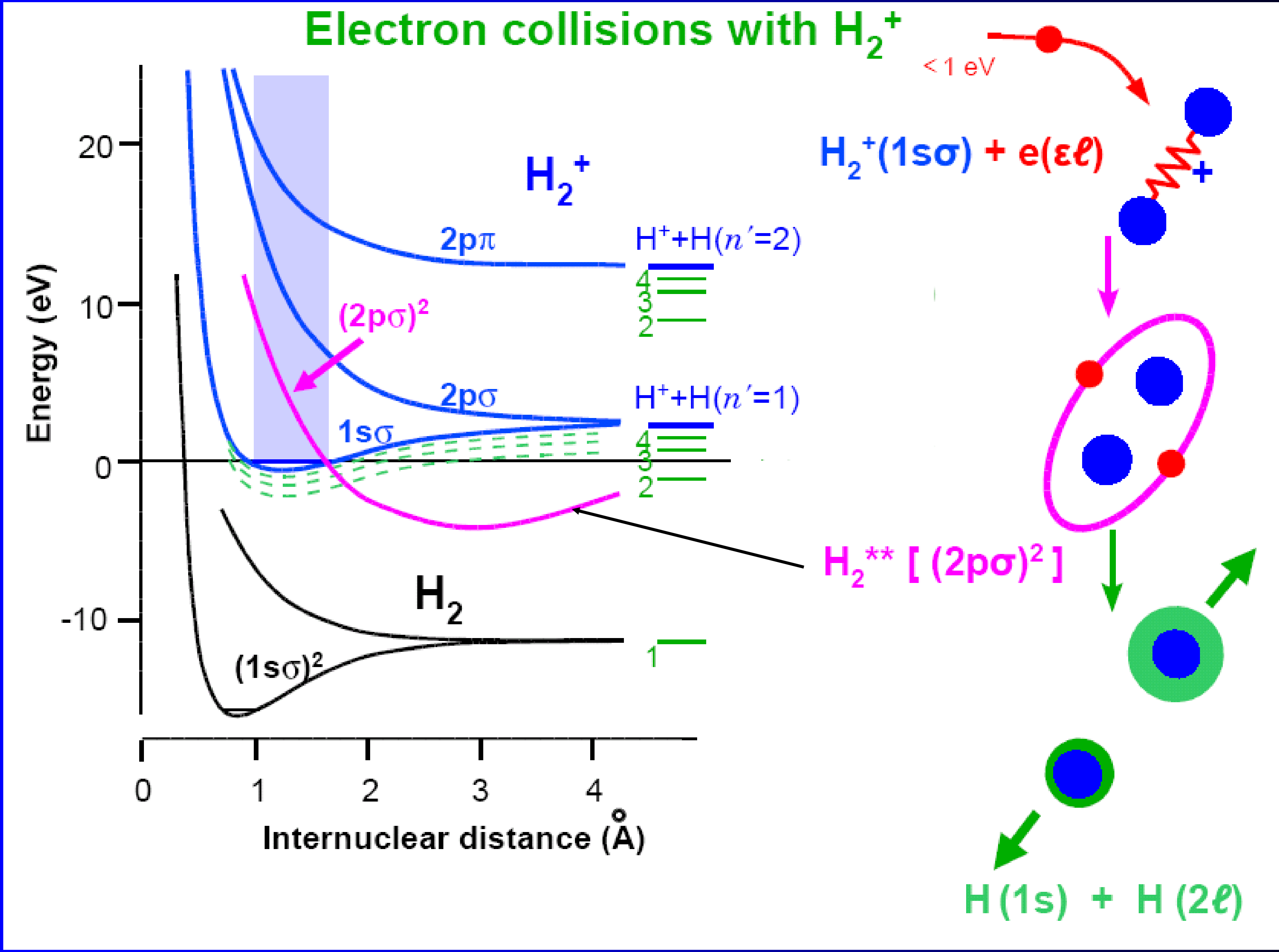
**The states involved: exemple for $He_2^+/He_2$ system**



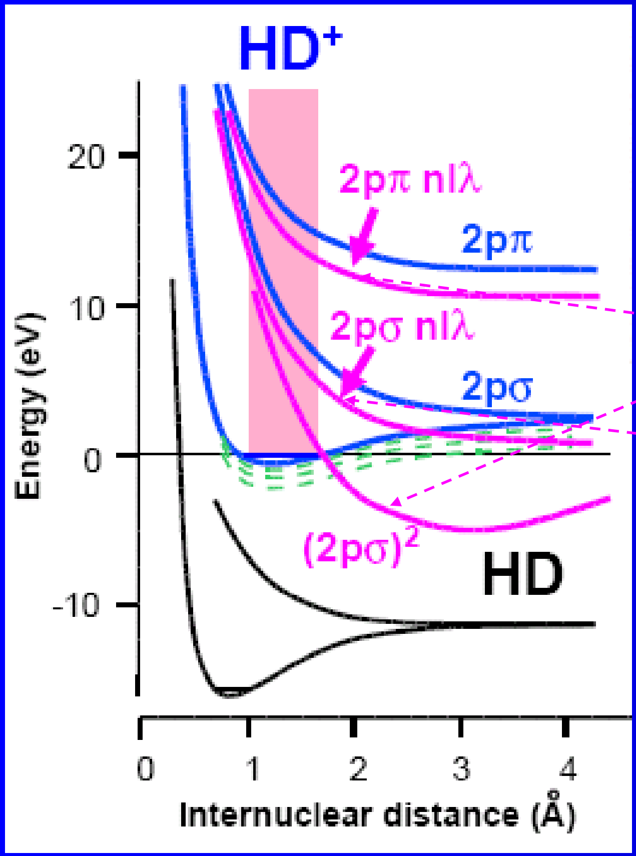

2004 DR6 Mosbach

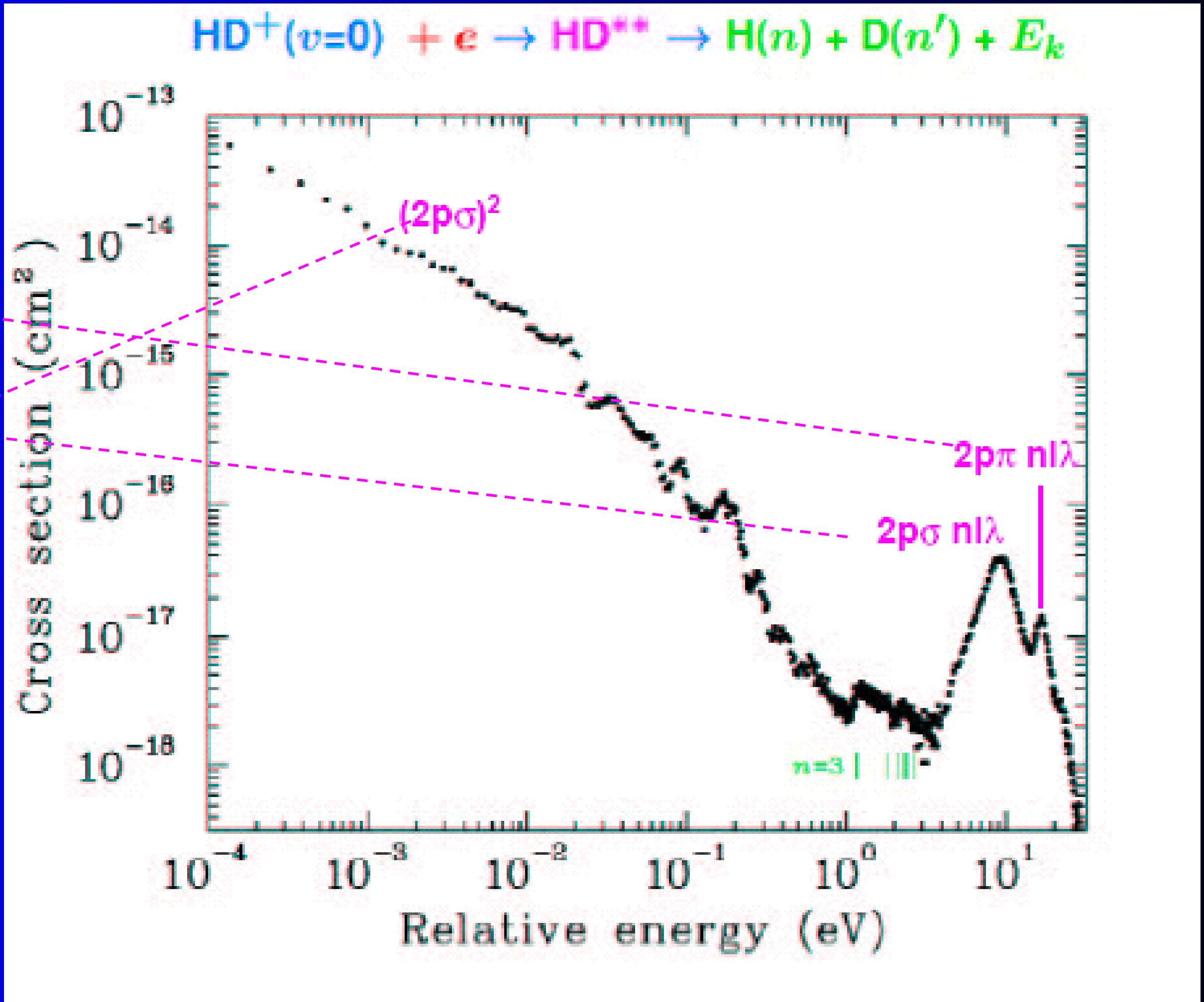
I. Schneider, et al., DR2004 Mosbach

# Electron - Ion Collision- Recombination



# Dissociative recombination



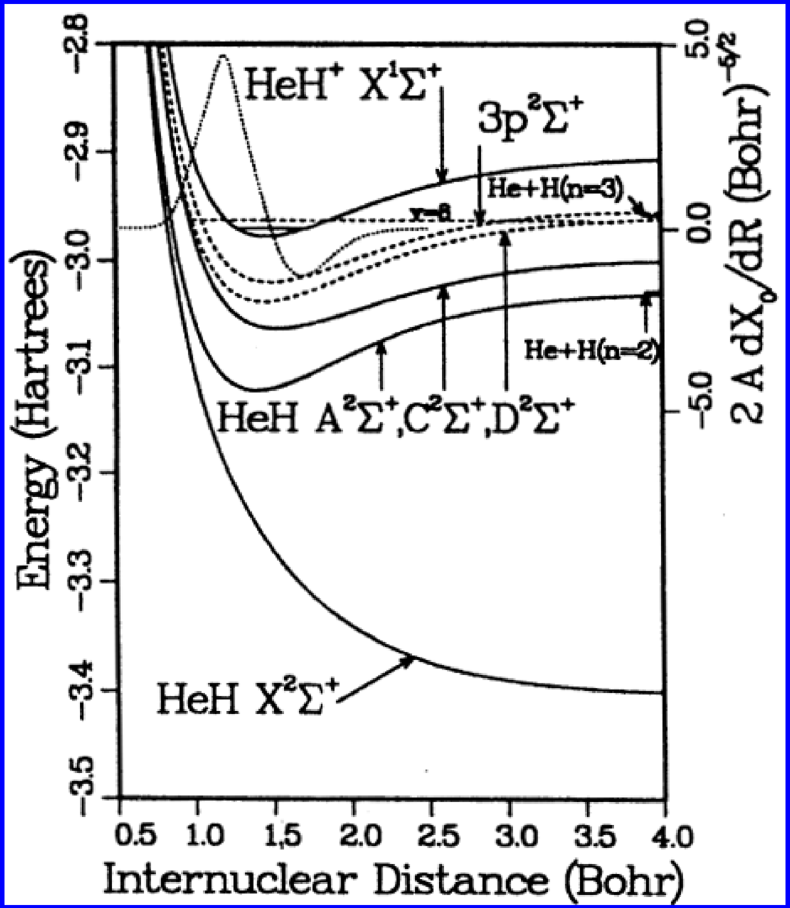




TSR: M. Lange et al., PRL 83 (1999) 4979;
Al-Khalili et al., PRA (2003)

# Theoretical background

## Dissociative Recombination without a Curve Crossing

Theory predicted: DR rate coefficient is vary small ~ $\mathbf{10^{-11}\ cm^3s^{-1}}$




$HeH^+$ and $HCO^+$ ions-
examples of a non-crossing case.
However, experiments gave
$\alpha \approx 2\times10^{-8}$ and $\alpha \approx 2\times10^{-7}$ $cm^3s^{-1}$

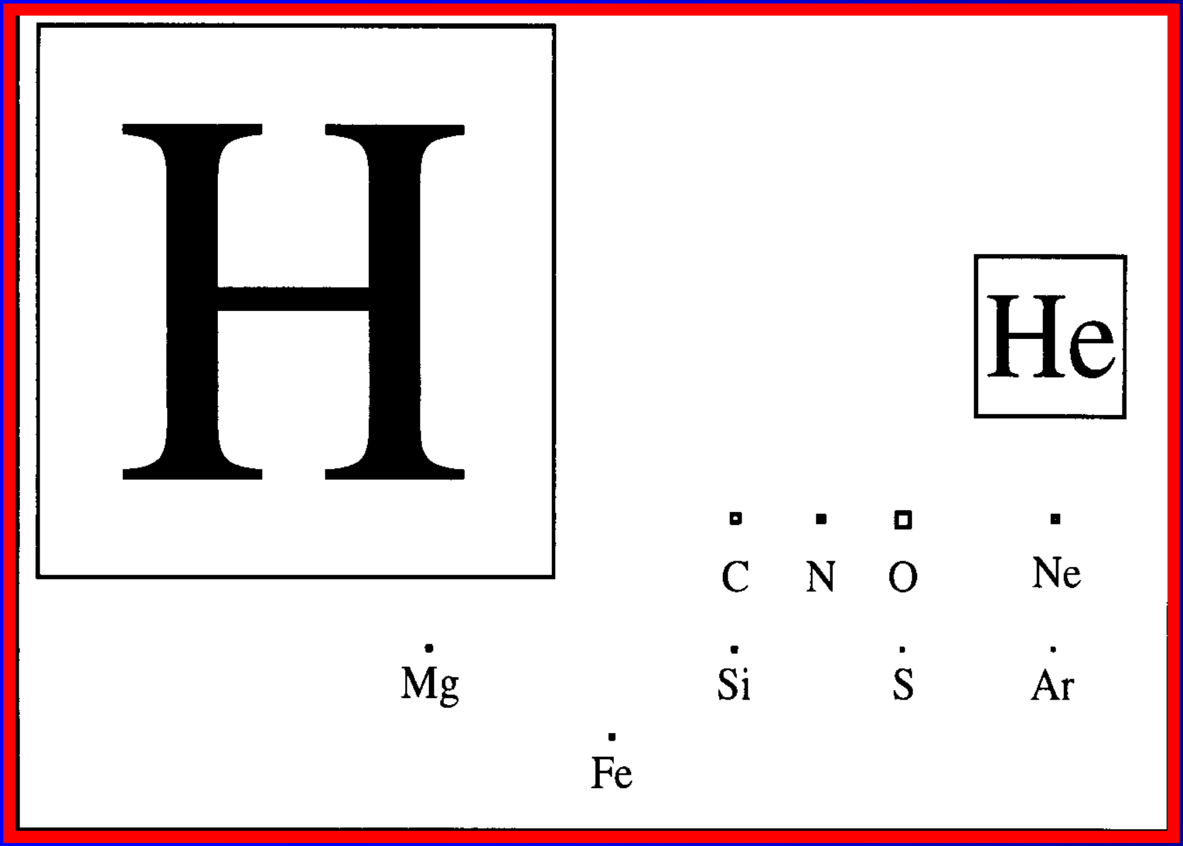
**A new mechanism has been proposed!**

Multi-step indirect
dissociative recombination
("tunneling mode" recombination)

# Interstellar medium

**92.1% of nucleons in the universe are protons**
**7.8% are helium nuclei !**
**0.1%……C,N,O,S,Si….**

**Cosmic abundance**

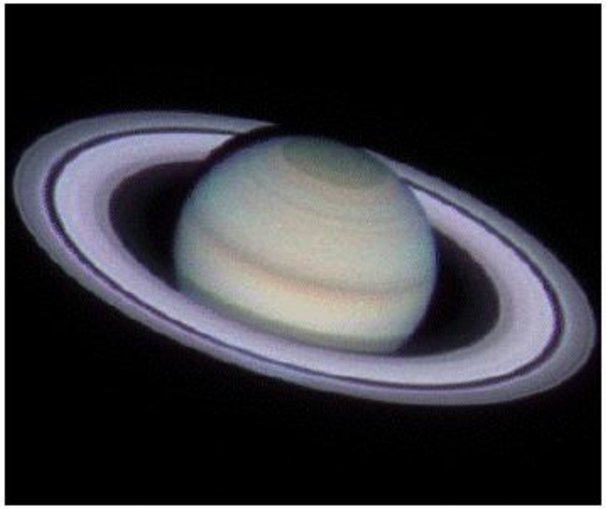



**~0.005%……D**

# Environments with H3+

Jupiter

Saturn



Uranus

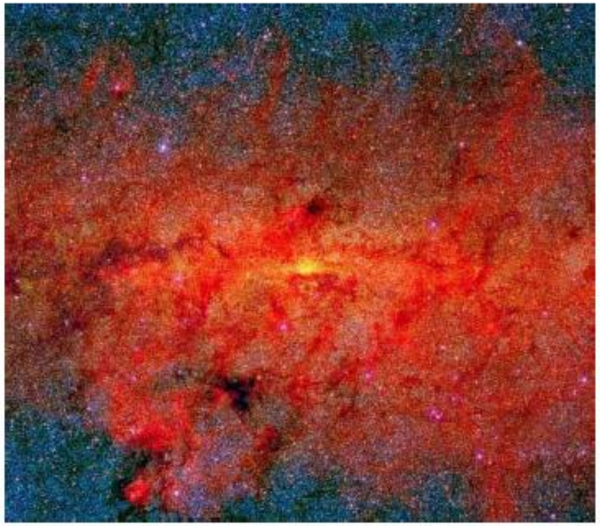
Dense Clouds

Barnard 68 (João Alves)

Diffuse Clouds

Cygnus OB2 (POSS)

Galactic Center



Galactic Center (2MASS/MSX)

# Interstellar medium

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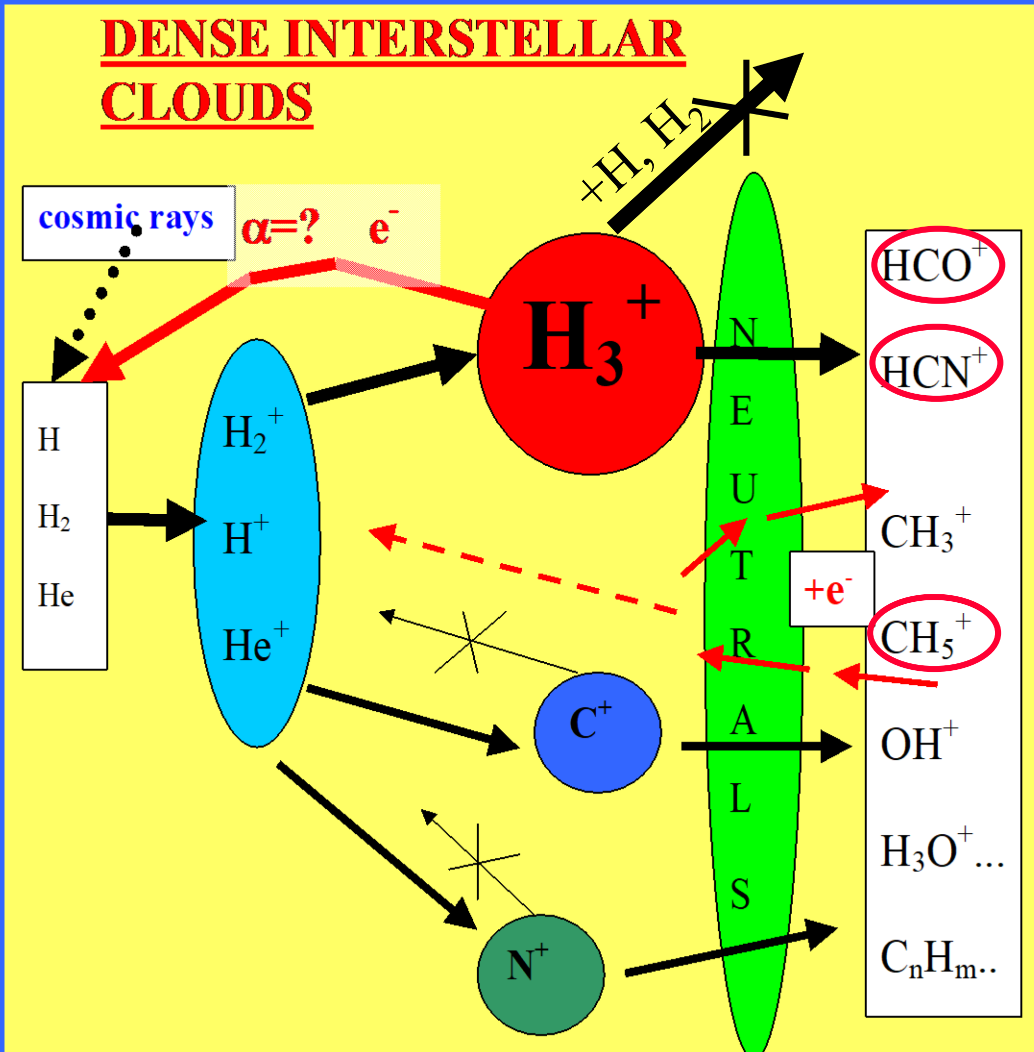


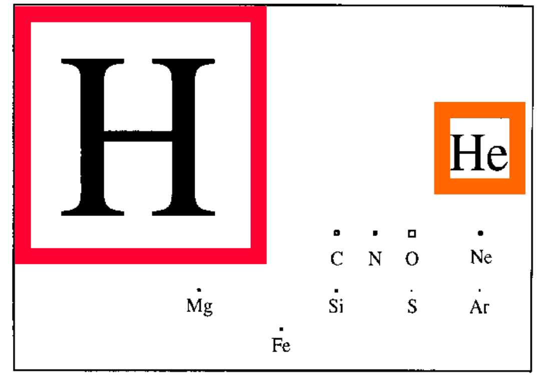



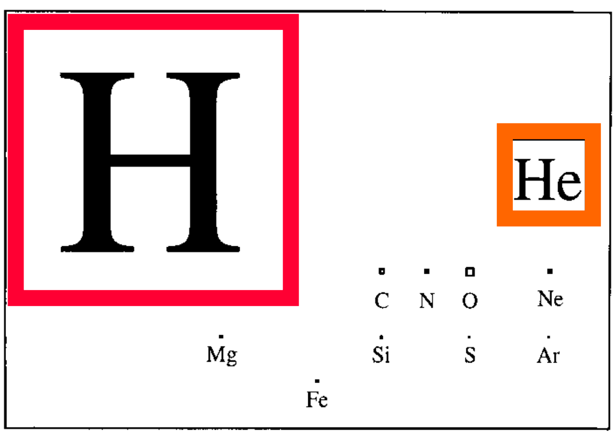

*Figure 1.* "The Astronomer's Periodic Table". The area of each element is proportional to its cosmic abundance.

$\alpha(T)$=???
@ 10-50K

$\sigma(v_r)$ =???
@ meV-eV

$$H_3^+ + e^- \Rightarrow H + H_2, 3H$$

**Experiments ???!!!**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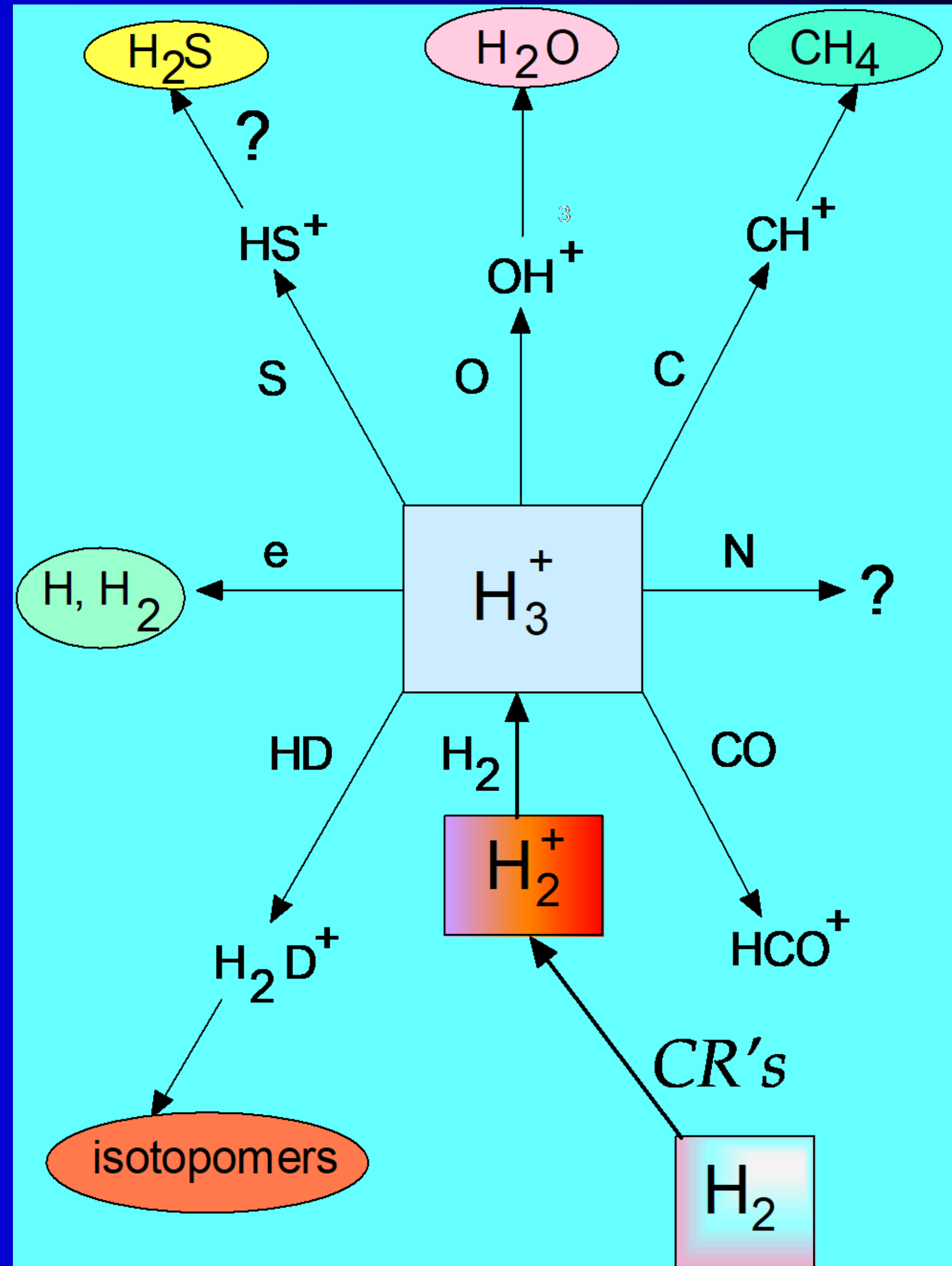


# Cosmic-ray ionisation rate $\gamma \sim 3 \times 10^{-17} s^{-1}$

Dense Clouds

Barnard 68 (João Alves)

**Formation**

$$H_2 \xrightarrow{h\nu} H_2^+ \xrightarrow{H_2} H_3^+$$

$$d[H_3^+]/dt \sim \gamma . [H_2]$$

Diffuse Clouds

Cygnus OB2 (POSS)

**a) DENSE CLOUDS:**

$H_3^+ + CO$ $\quad d[H_3^+]/dt \sim -k_{CO} x[H_3^+] x[CO]$

$(k_{CO} = 2 \times 10^{-9} cm^3 s^{-1})$

$[H_3^+] = \gamma / k_{CO} \, . \, [H_2]/[CO] =$ **$\sim 1 \times 10^{-4} cm^{-3}$**

**~OK with observation**

**b) DIFFUSE CLOUDS:**

$H_3^+ + e^-$ $\quad d[H_3^+]/dt \sim - \alpha_{DR} [H_3^+][e^-]$

$\alpha_{DR} = 2 \times 10^{--7} cm^3 s^{-1} \, x(T/300)^{-0.65}$ (the value from 2005)

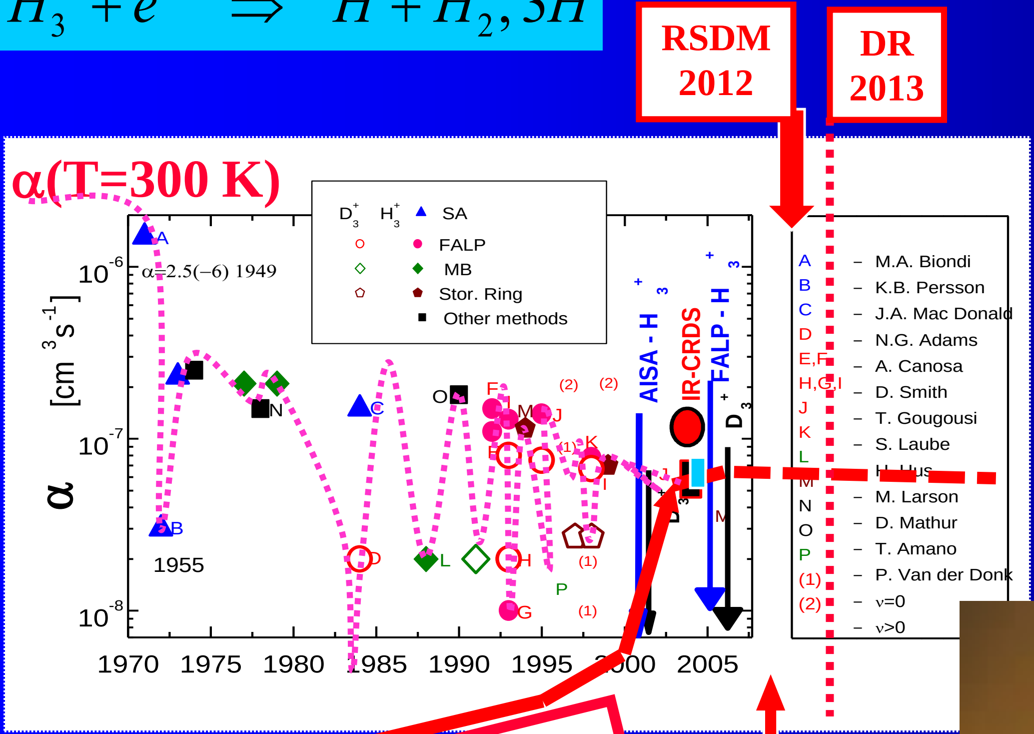
$[H_3^+] = \gamma / \alpha_{DR} \, . \, [H_2]/[C] =$ **$\sim 1 \times 10^{-7} cm^{-3}$**

**~ NO with observation**

History of experiments

# … history is repeating itself ….

$H_3^+ + e^- \;\Rightarrow\; H + H_2, 3H$



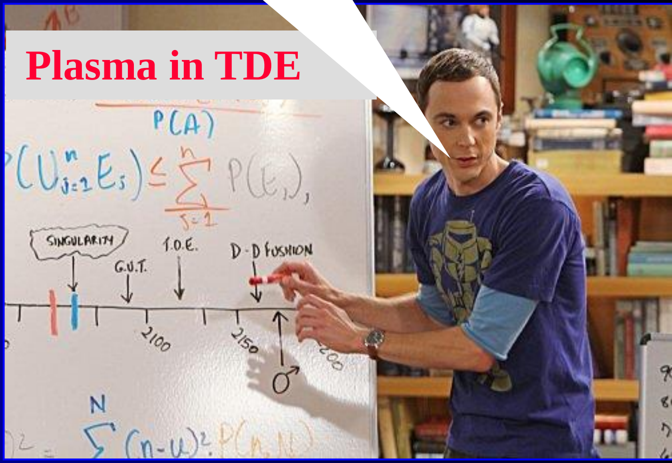

**"Presently no rate coefficient measurement with a confirmed temperature below 300 K exists".**

Petrignani *et al*. Phys. Rev. A (2011)

***and … history repeated itself .***

M. Larsson et al, CP Letters (2008)

***… One remaining problem is to understand the plasma afterglow experiments.***

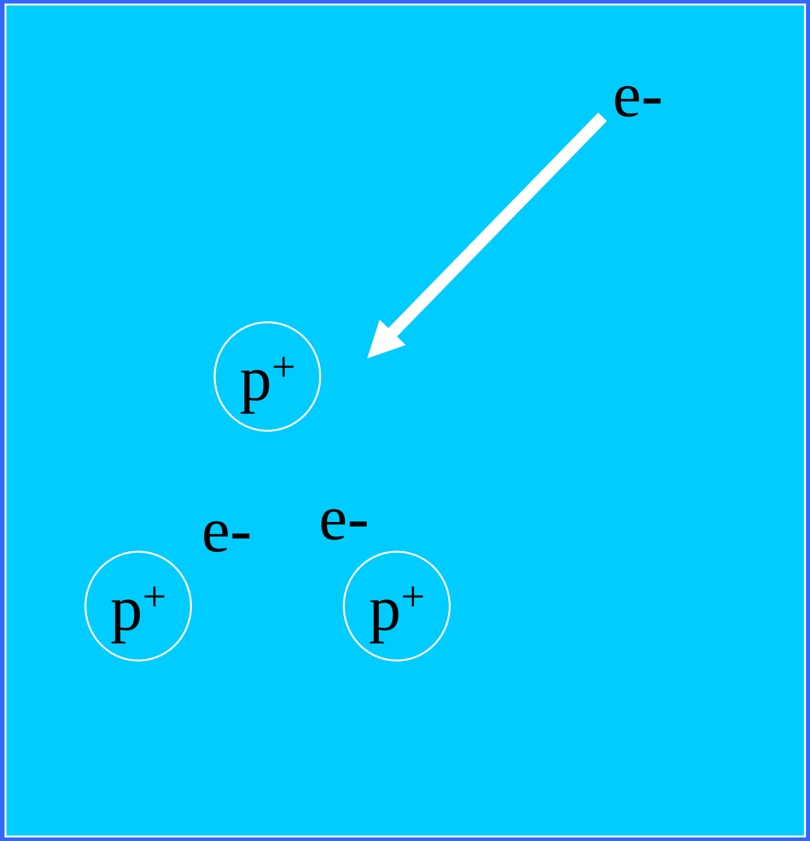



…. many times it was concluded, that the task was finished….

… and the caravan is on its way

p/o

# Recombination of $H_3^+$



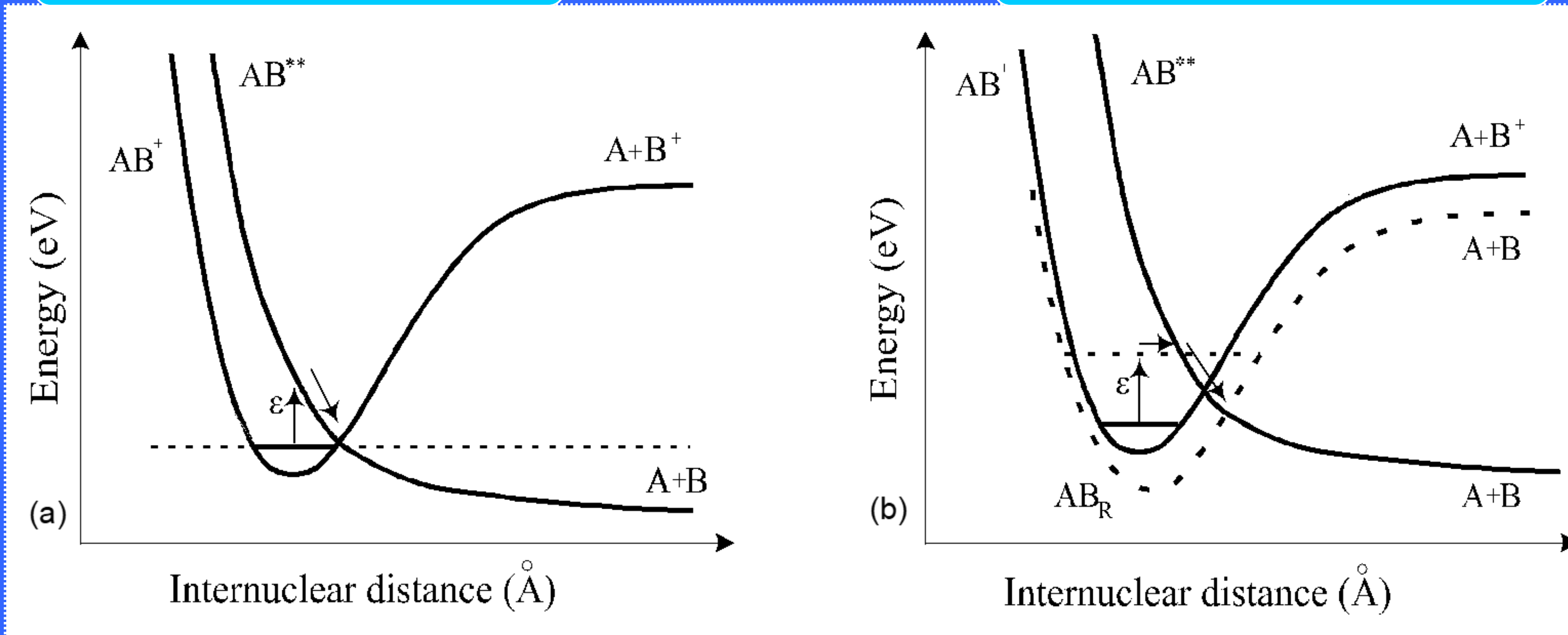

$$H_3^+ + e^- \rightarrow H+H+H$$

$$\rightarrow H_2+H$$

$$\rightarrow H_3^* \quad (?)$$

## Direct DR process

## Indirect DR process




$$AB^+ + e^- \underset{k_{auto}}{\overset{k_c}{\rightleftarrows}} AB^{**} \xrightarrow{k_{stab}} A + B$$

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# Tunneling dissociative recombination

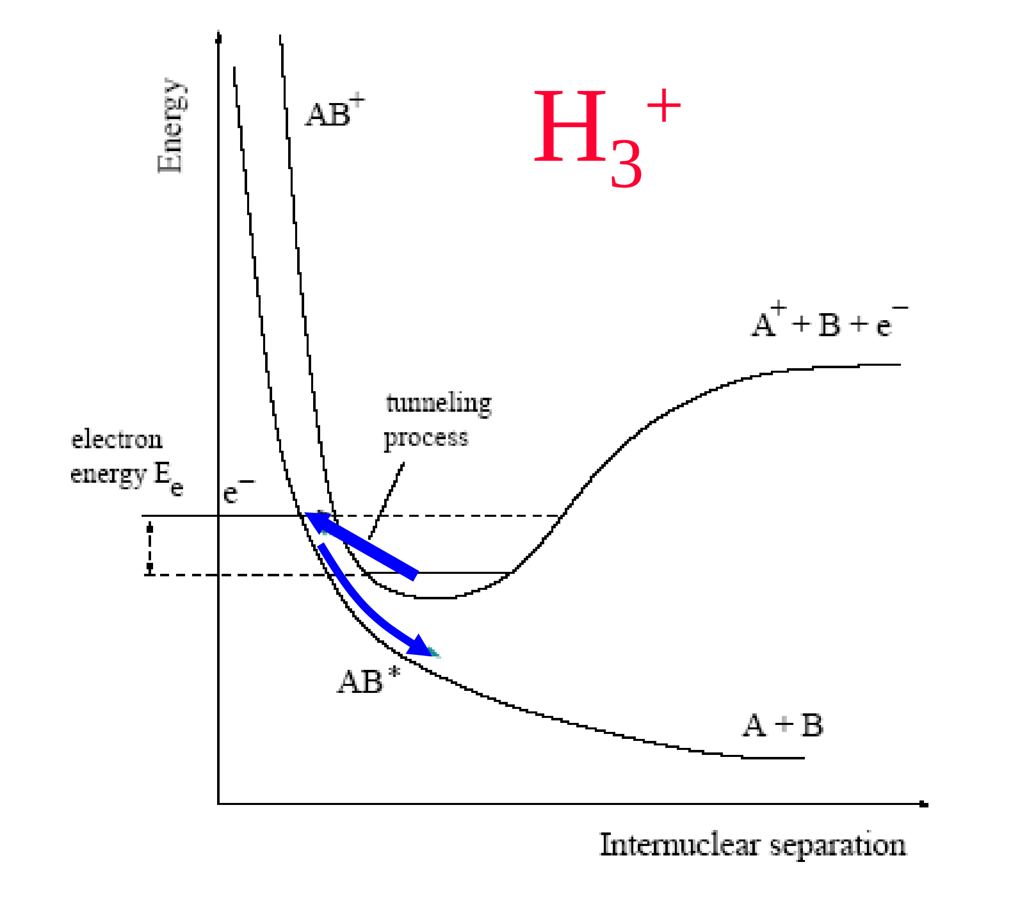
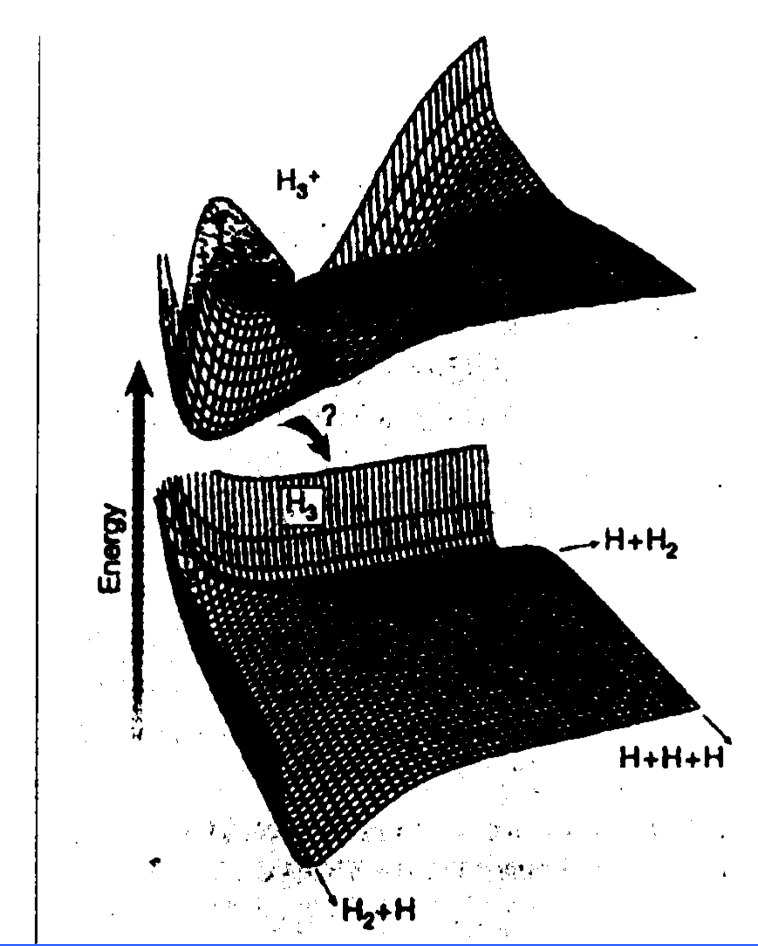



**Figure 4.3:** *Sketch of tunneling mode dissociative recombination.*



# $H_3^+$ Potential curves

**In the case of $H_3^+$, a simple 2-dimensional picture of molecular states suggests that recombination should be very inefficient**

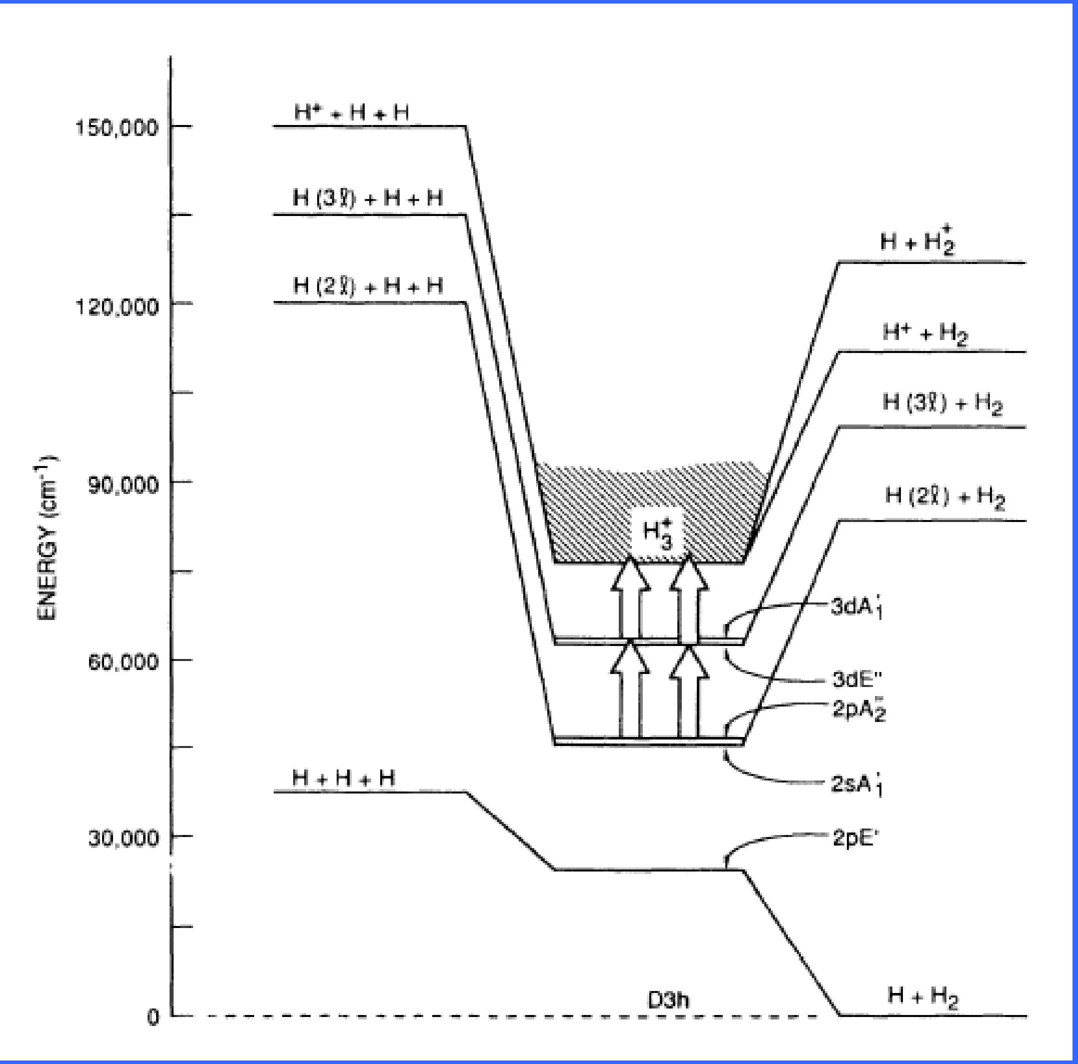
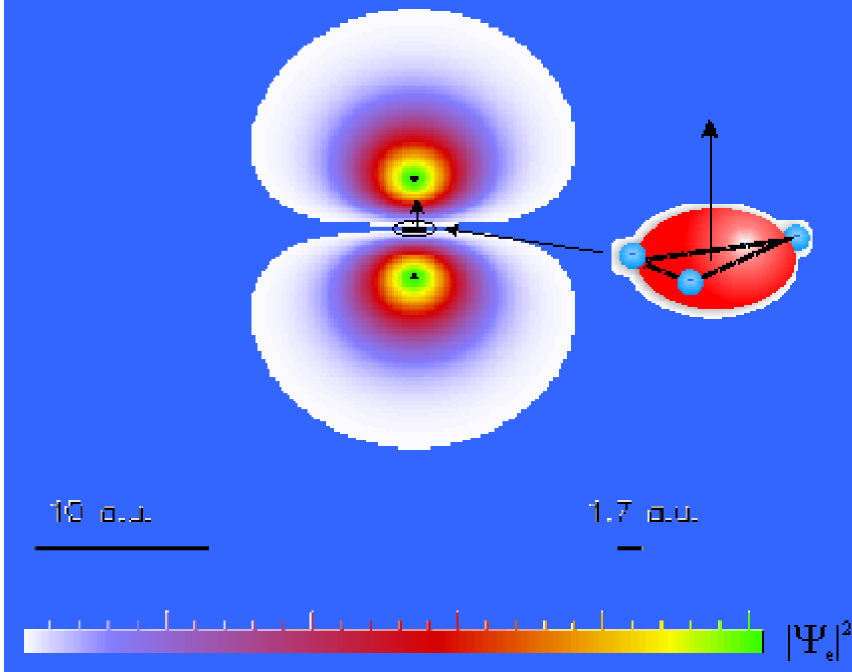
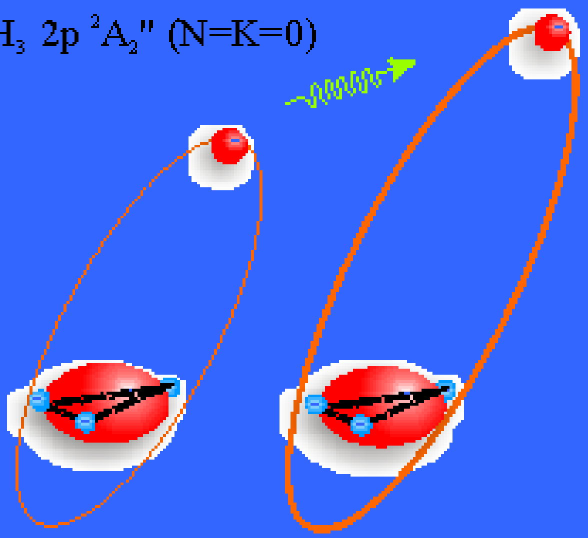


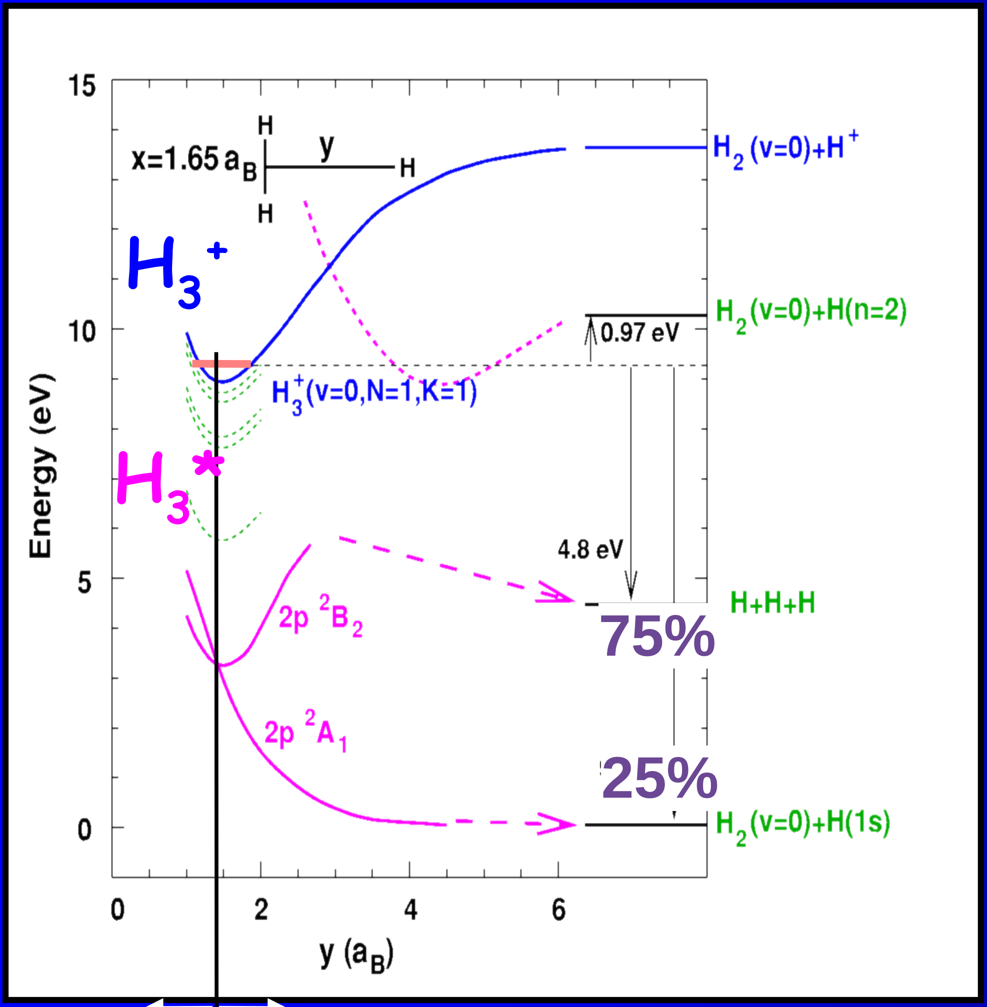

FIG. 1. Energy diagram of triatomic hydrogen ($D_{3h}$ geometry) showing the location of the bound Rydberg states and the unstable ground state of $H_3$ in relation to the neutral and ionic dissociation limits.



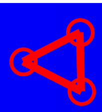

Metastable: $H_3$ 2p $^2A_2''$ (N=K=0)



# Dissociative recombination of $H_3^+$




Symmetric deformation

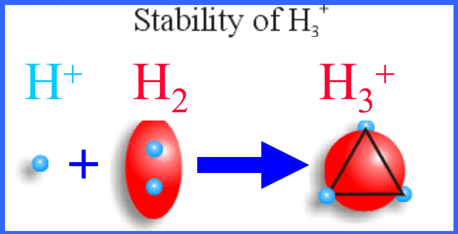


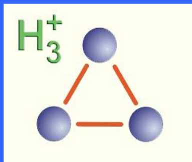
Remote curve crossing

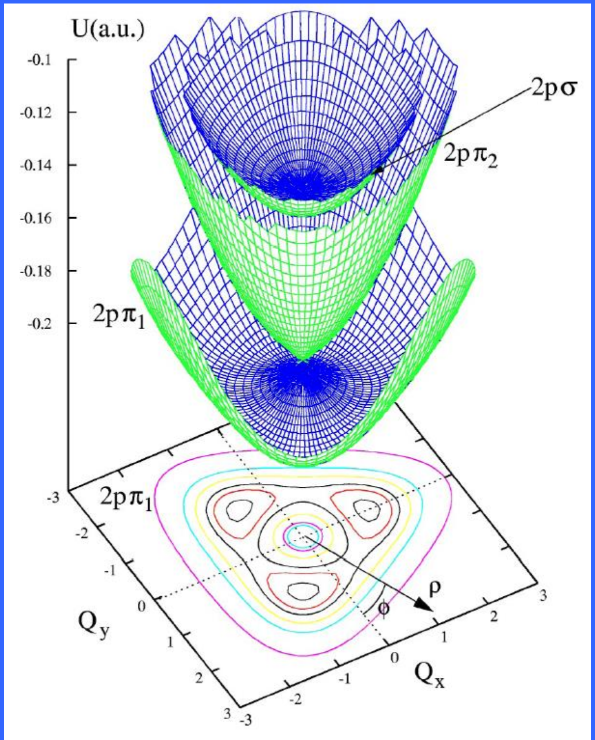
Electron capture via Jahn-Teller coupling of electronic and ro-vibrational motion

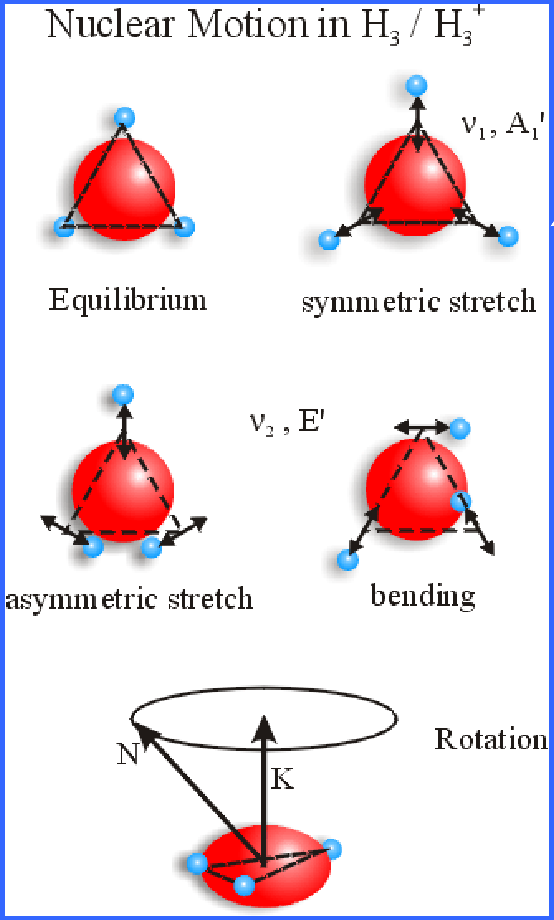
*Prototype system* for electron capture and dissociation mechanisms in polyatomic species

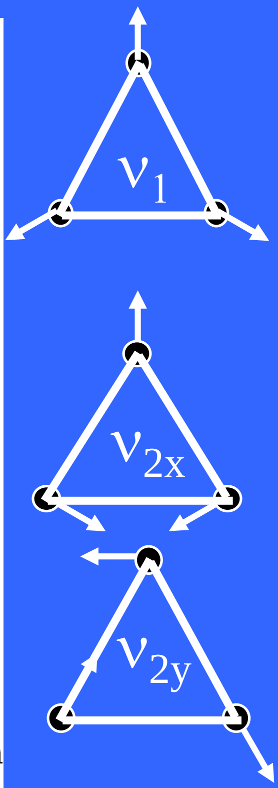
# $H_3^+(v=0)$ molecular ion



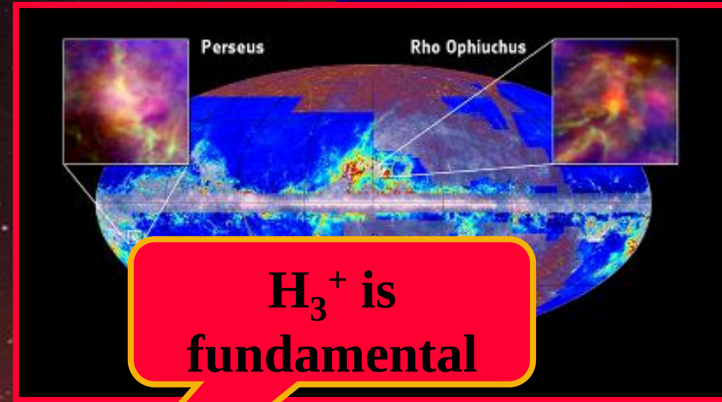

# Formation

$$H_2^+ + H_2 \xrightarrow{k} H_3^+ + H$$

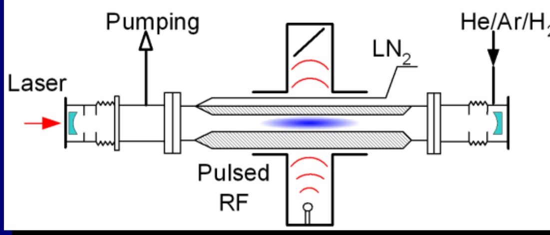
$$ArH^+ + H_2 \xrightarrow{k} H_3^+ + Ar$$

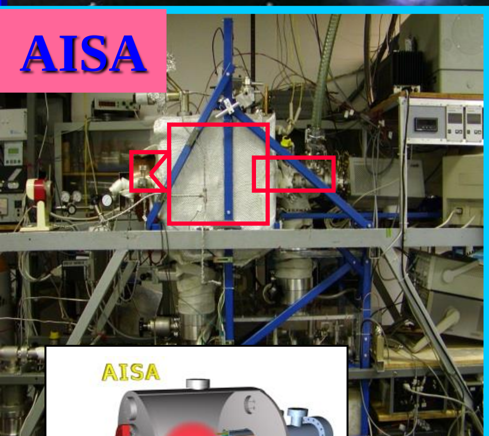
$$H^+ + H_2 + He \underset{k_{-3}}{\overset{k_3}{\leftrightarrow}} H_3^+ + He$$

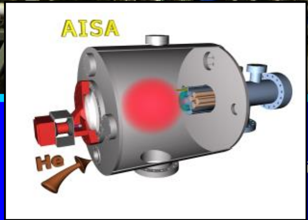
# The battle ship enters the stage

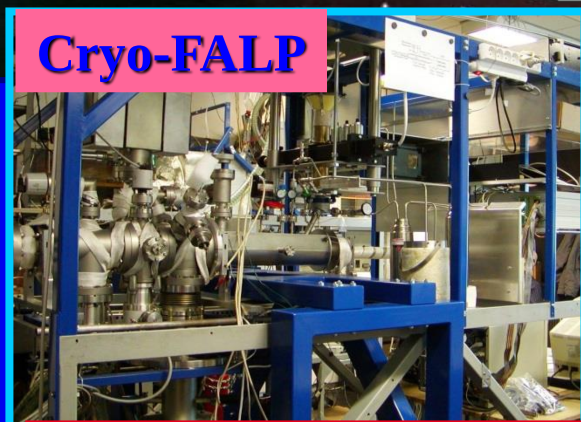



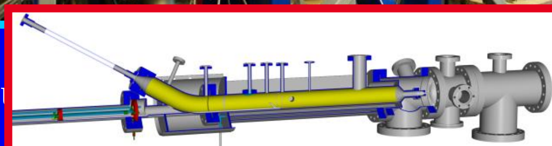




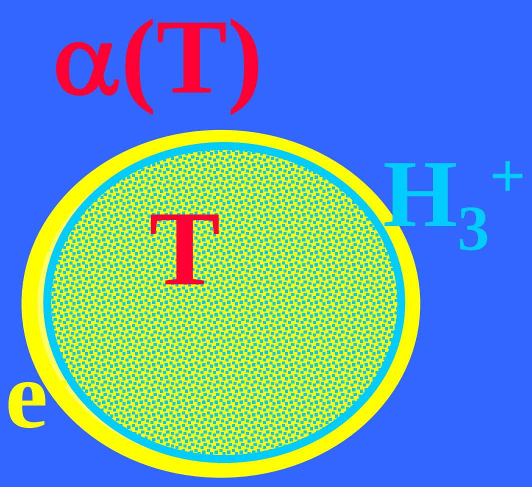
versity Pragu

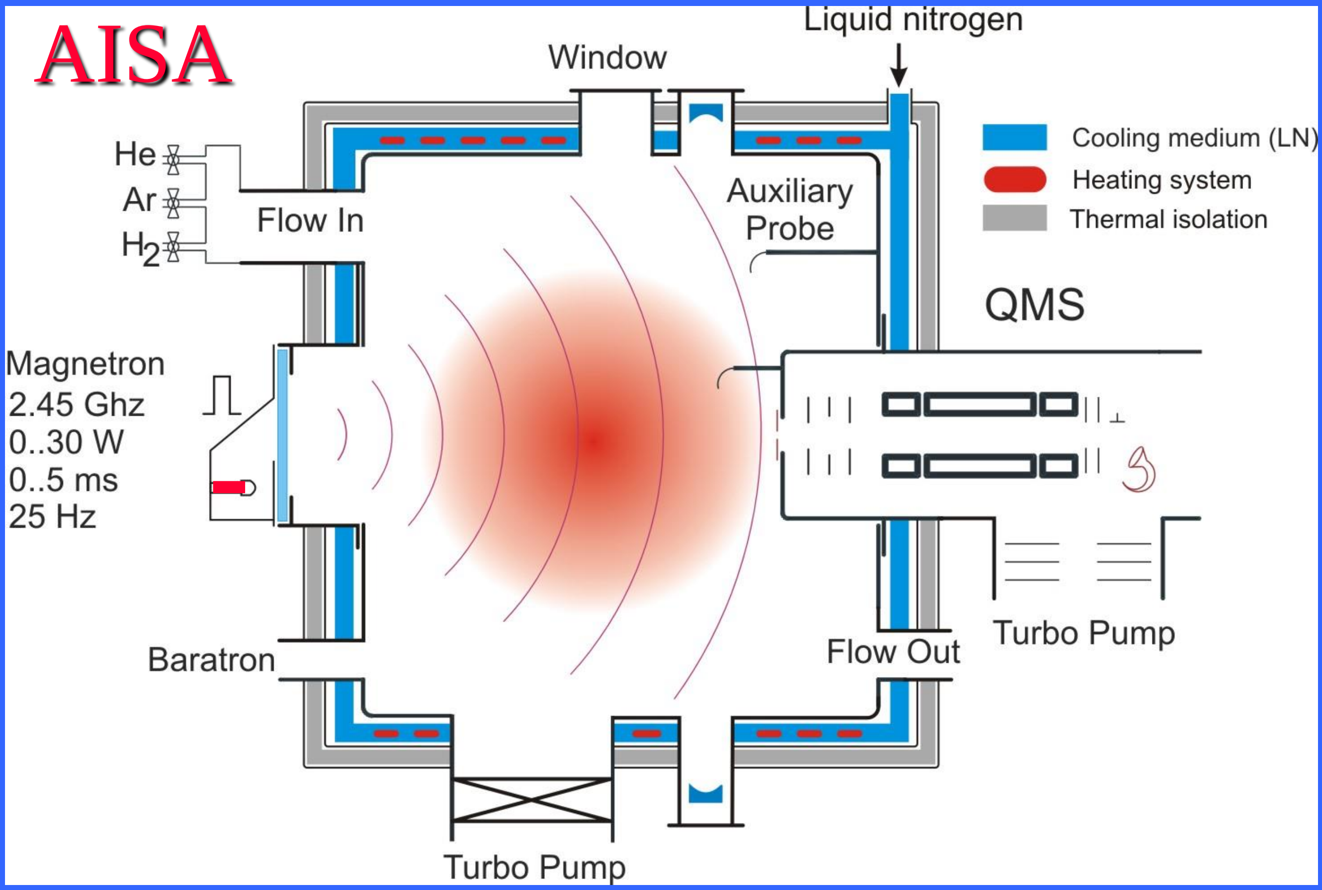
Pressure dependence

# VT - AISA

$dn_i/dt=-\alpha n_i n_e$

$He/Ar/H_2$

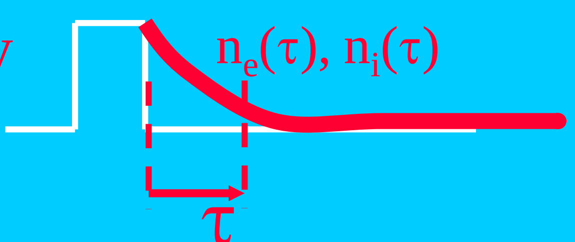


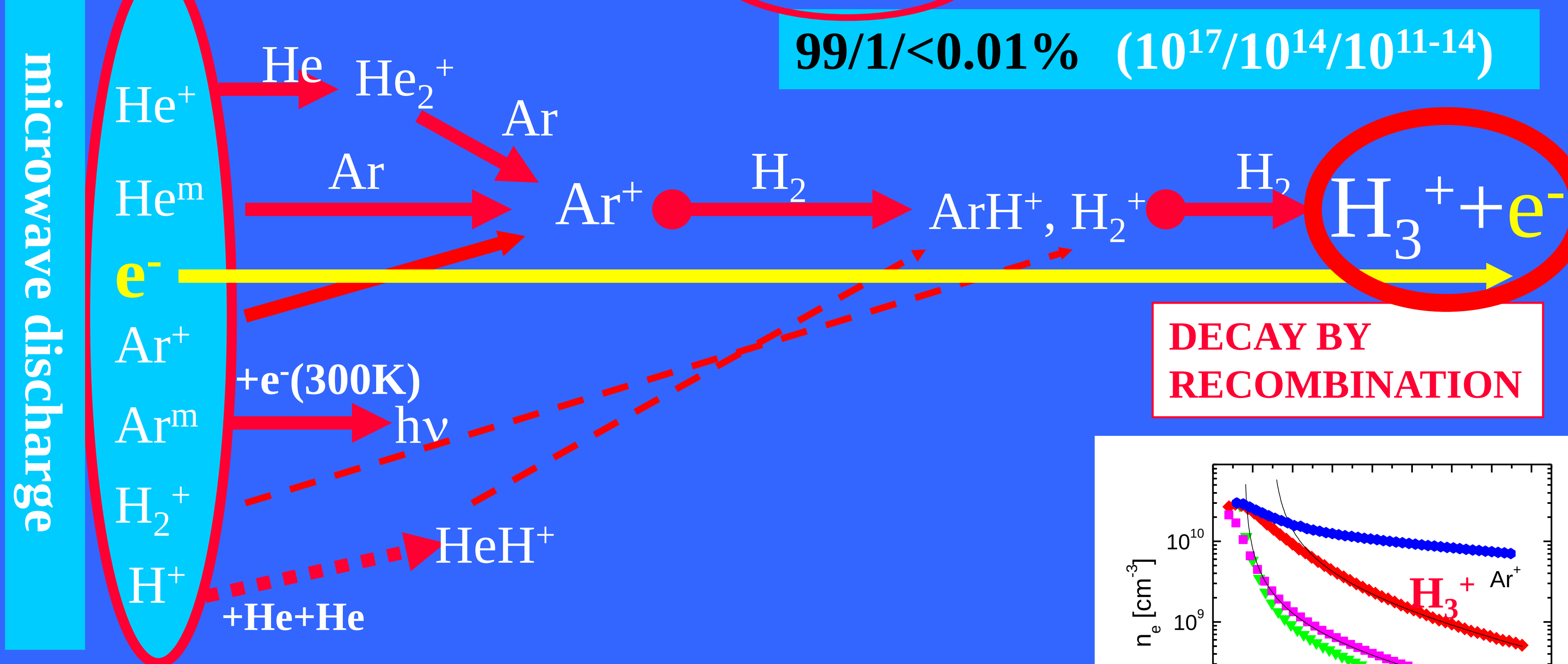

**40 cm diameter**
**UHV - $10^{-9}$ Torr**
**External magnetron**
**2 Torr of $He/Ar/H_2$**

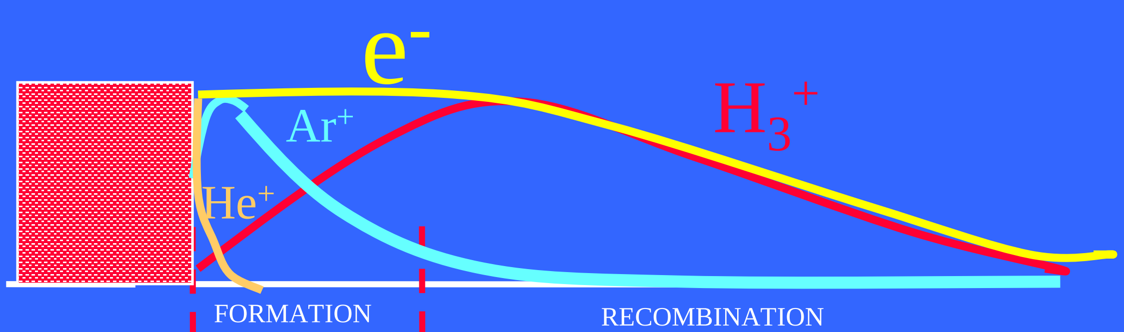
PULSED STATIONARY AFTERGLOW

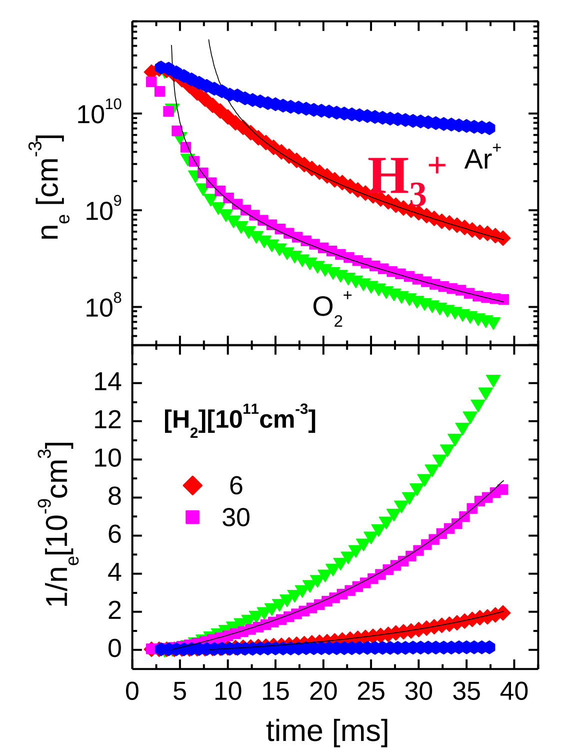
20-100ms decay



# Formation of $H_3^+$ in He/Ar/$H_2$



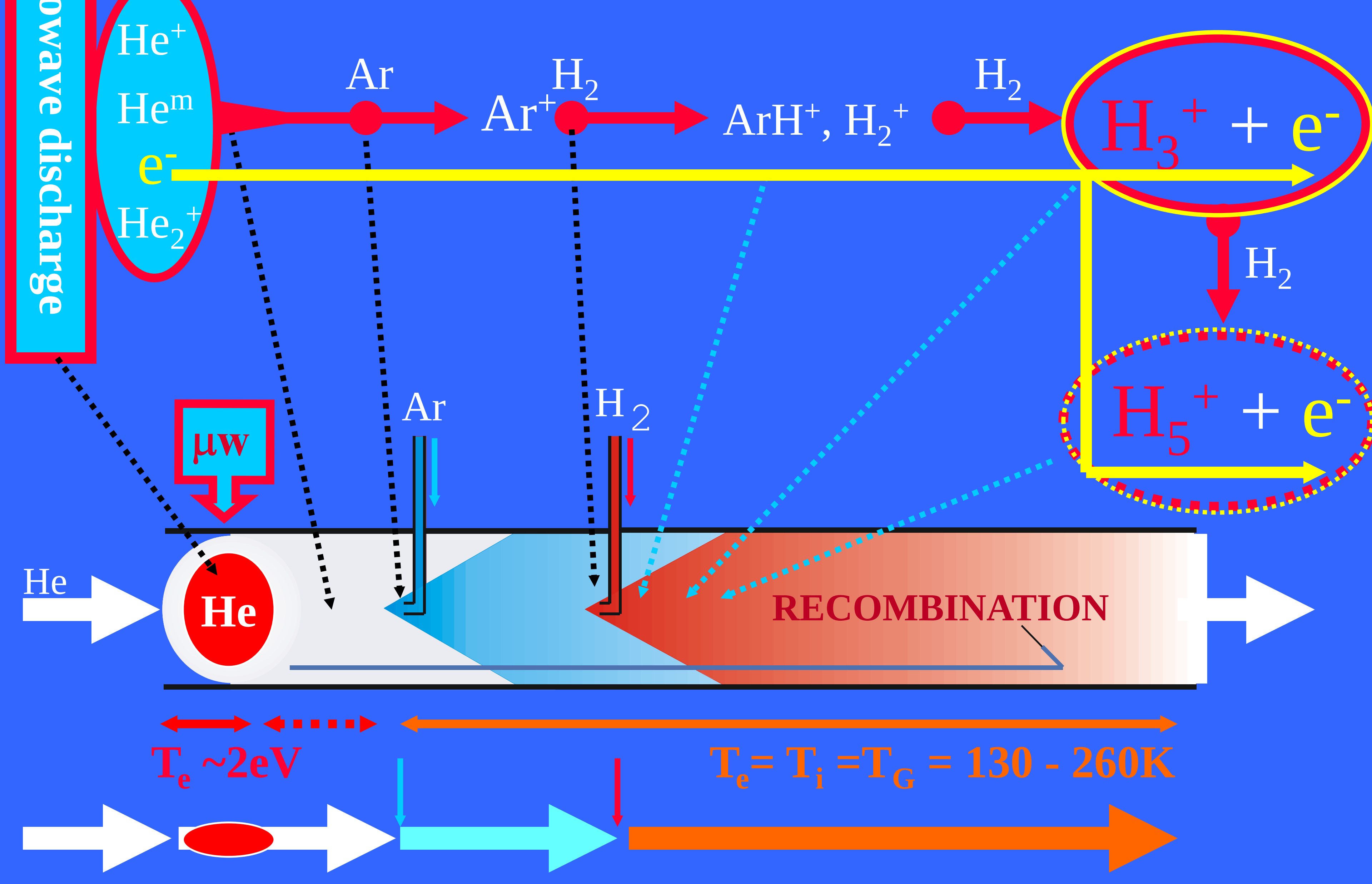




Time resolved mass spectra

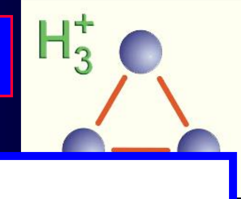
# FALP – Flowing Afterglow Langmuir Probe

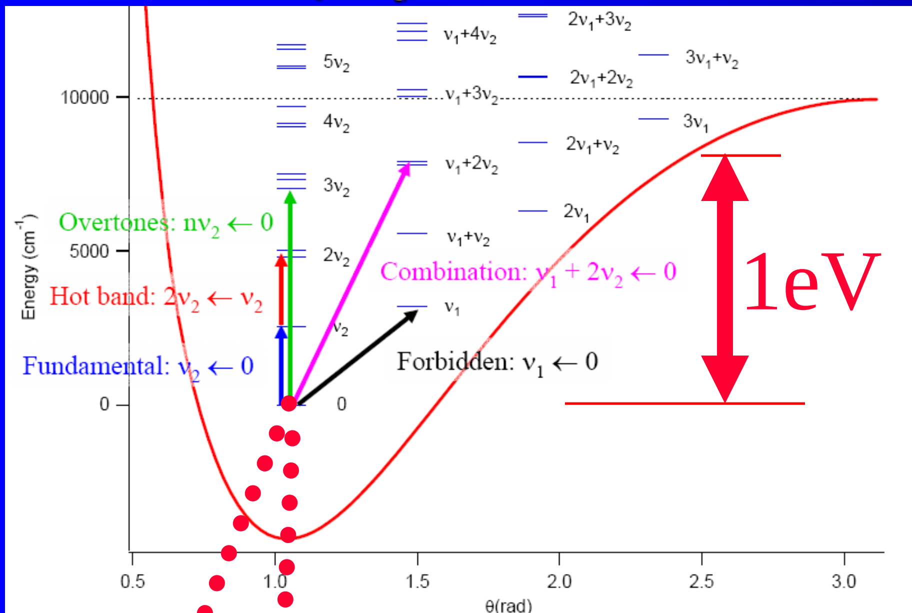
Formation of $H_3^+$ in He/Ar/$H_2$ mixture (10 Torr)

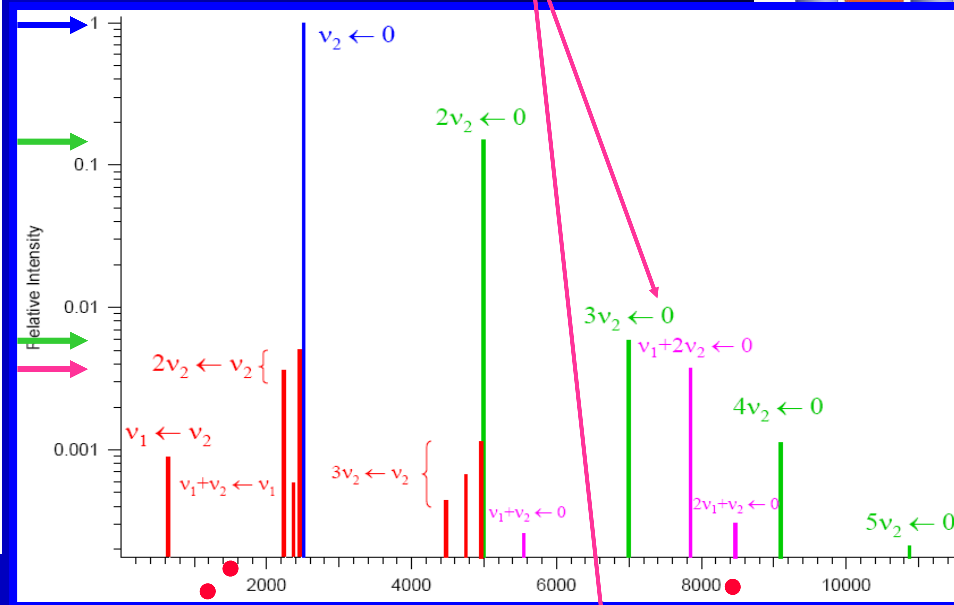


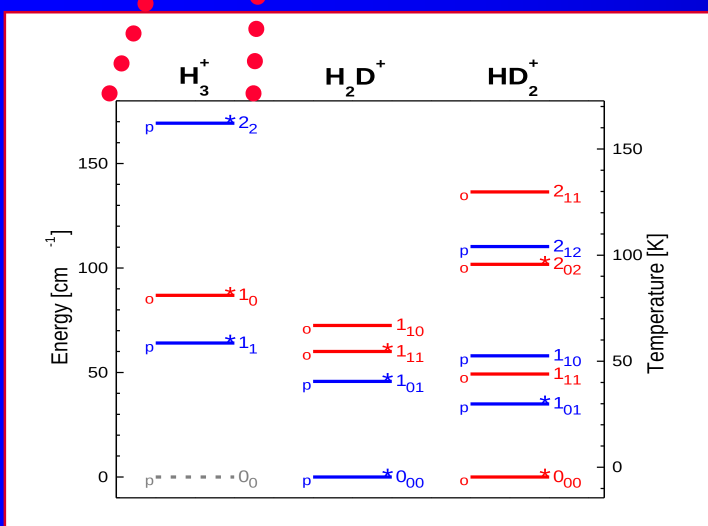
# Line intensity $H_3^+$

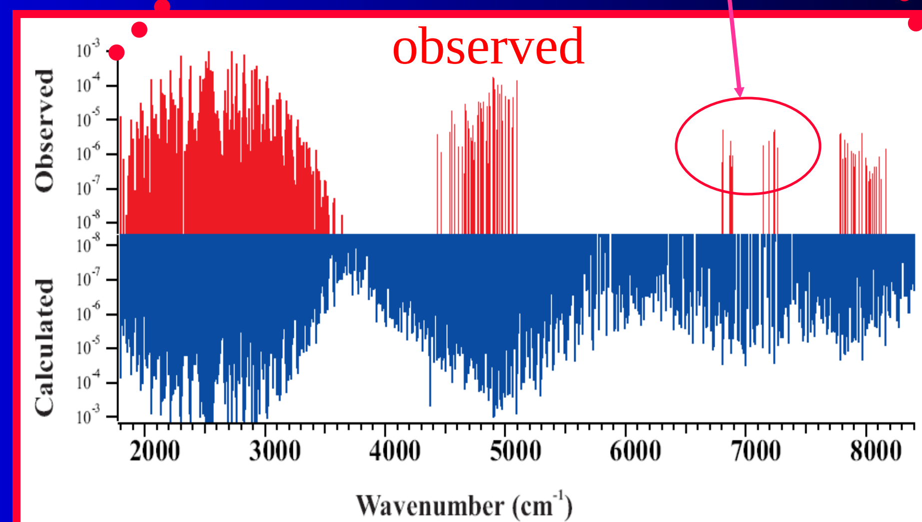
High sensitivity required



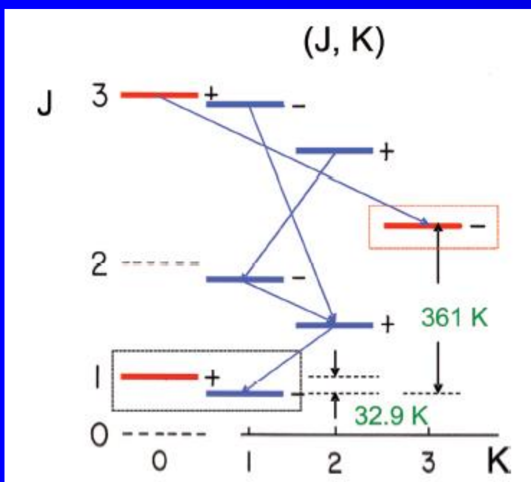



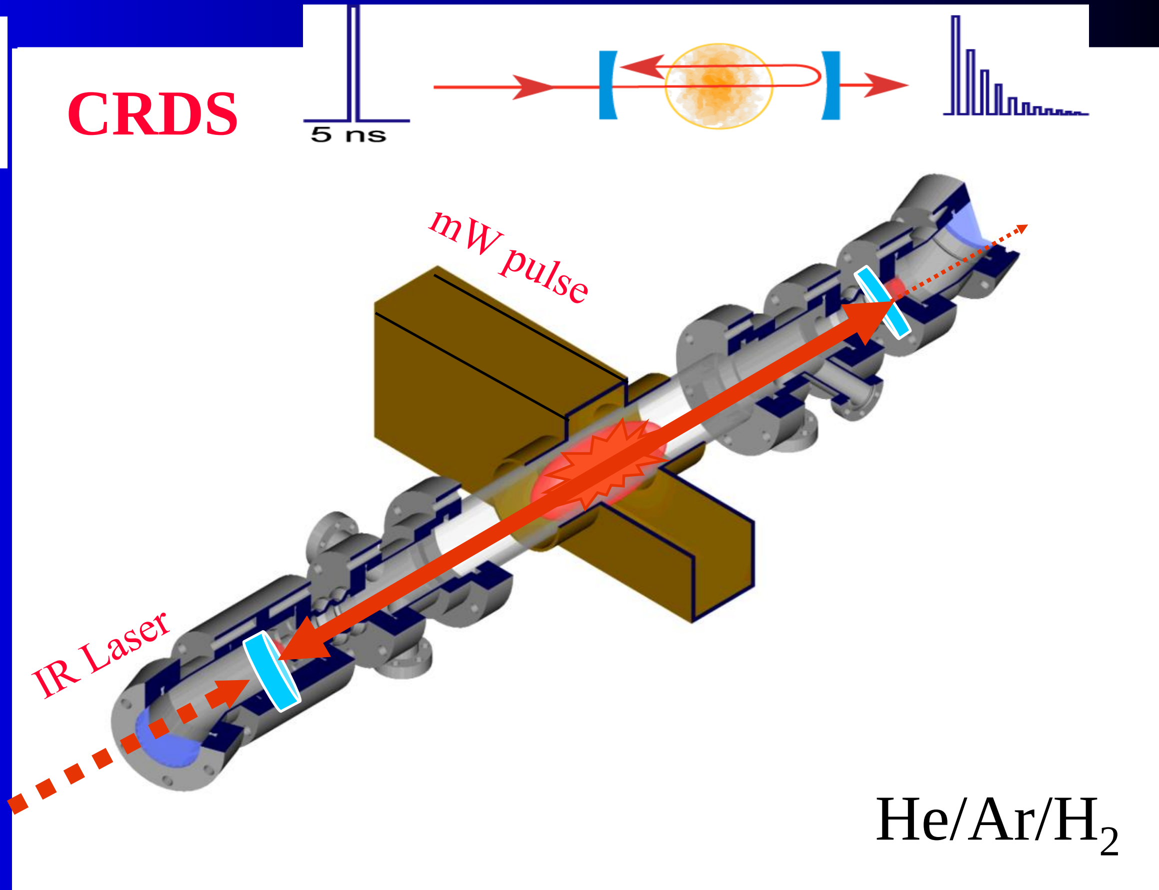
# Stationary afterglow + Spectroscopic identification of recombining ions

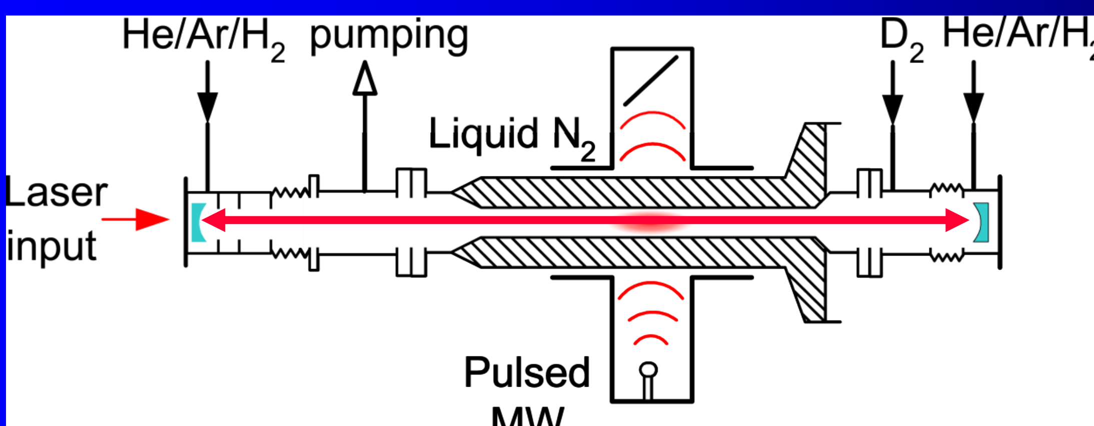
$$\frac{d[H_3^+]}{dt} = -\alpha[H_3^+]n_e = -\alpha[H_3^+]^2$$

IR-CRDS

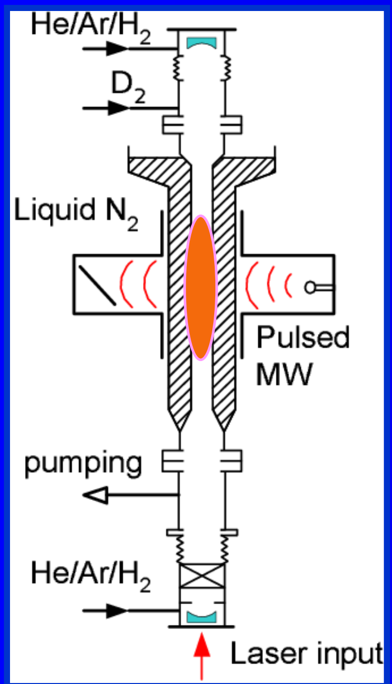
Laser absorption spectroscopy

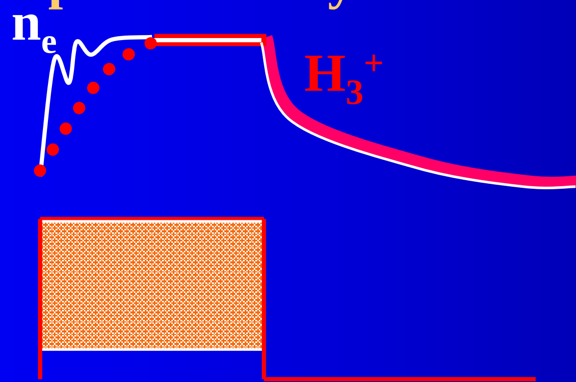


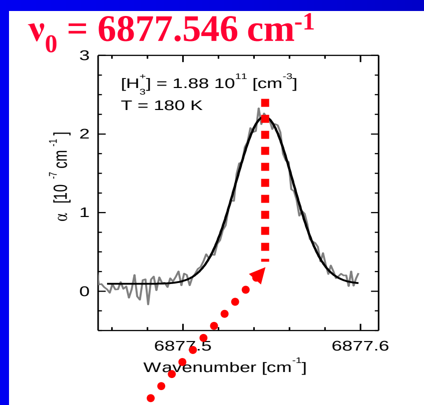



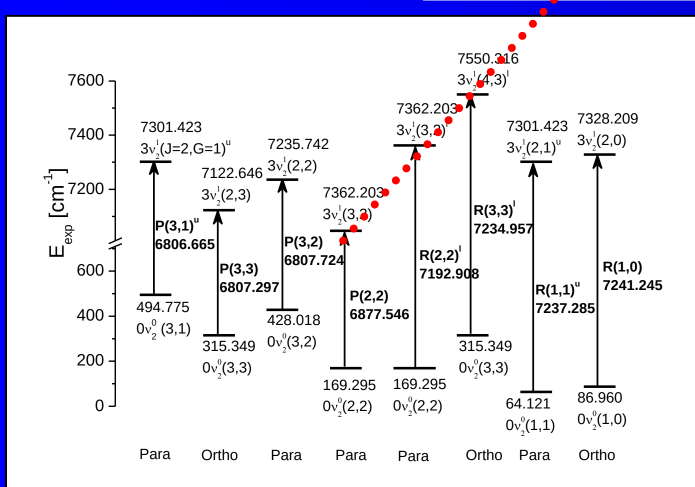



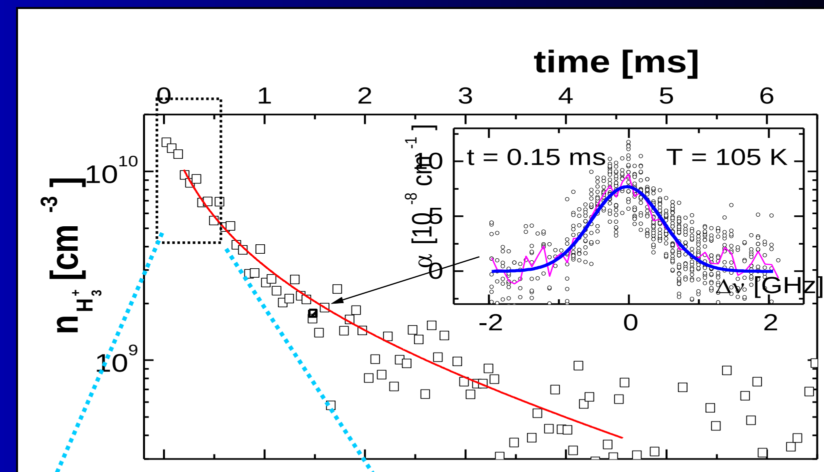
# Pulsed discharge – plasma decay



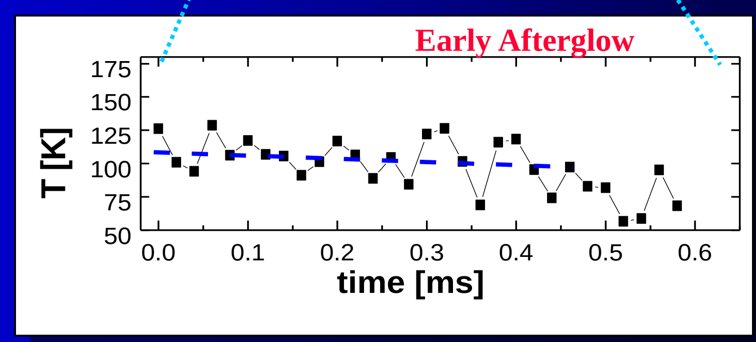



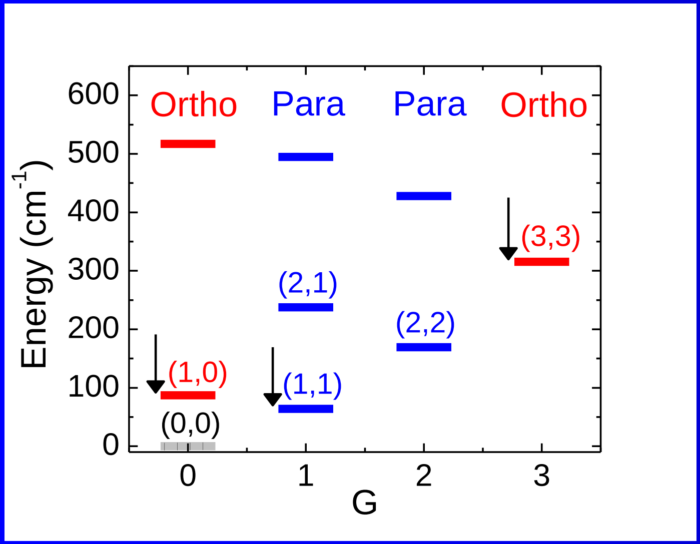



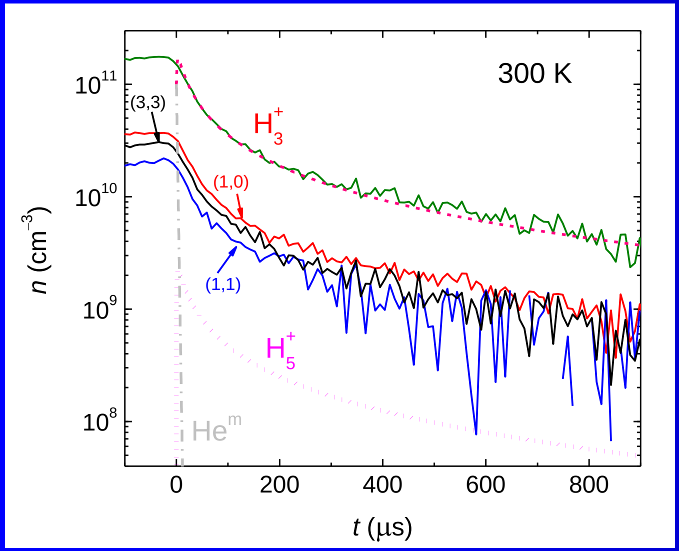




From Doppler broadening

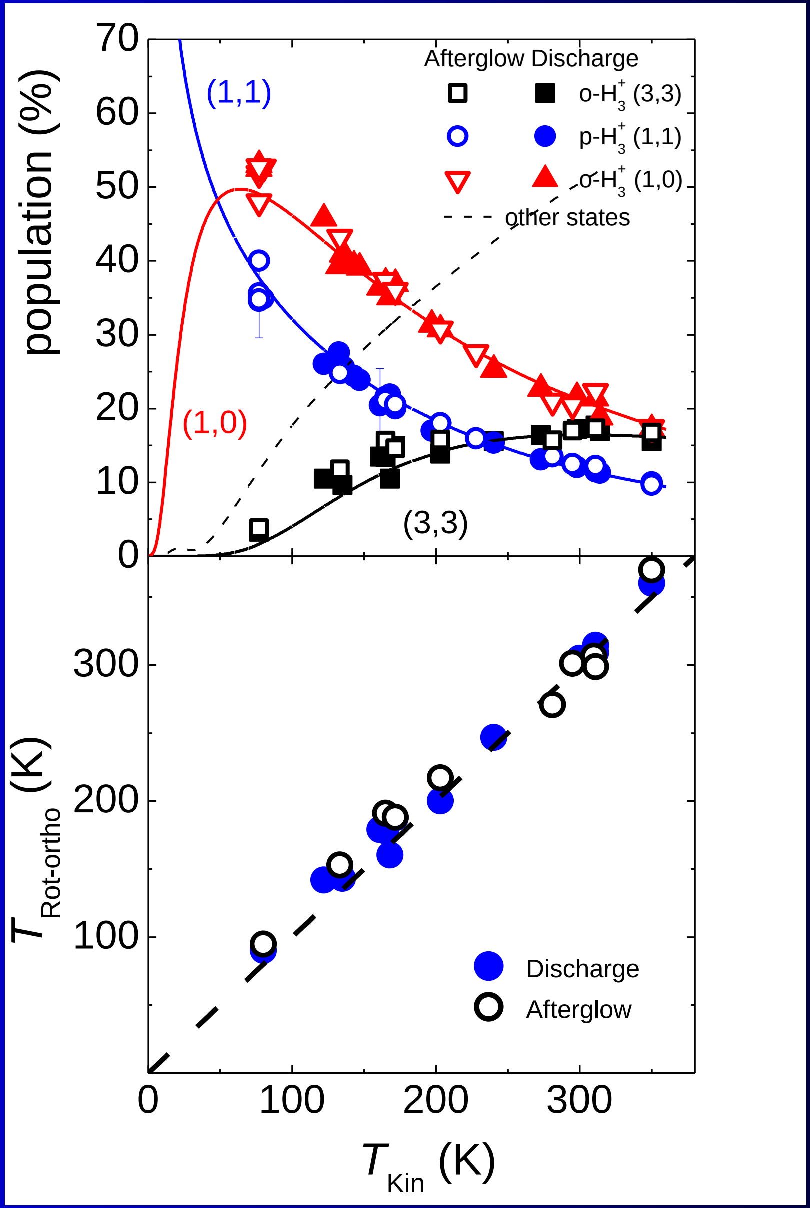




Ortho
Para
Para
Ortho
(3,3)
(2,1)
(2,2)
(1,0)
(1,1)
(0,0)
Energy (cm$^{-1}$)
G

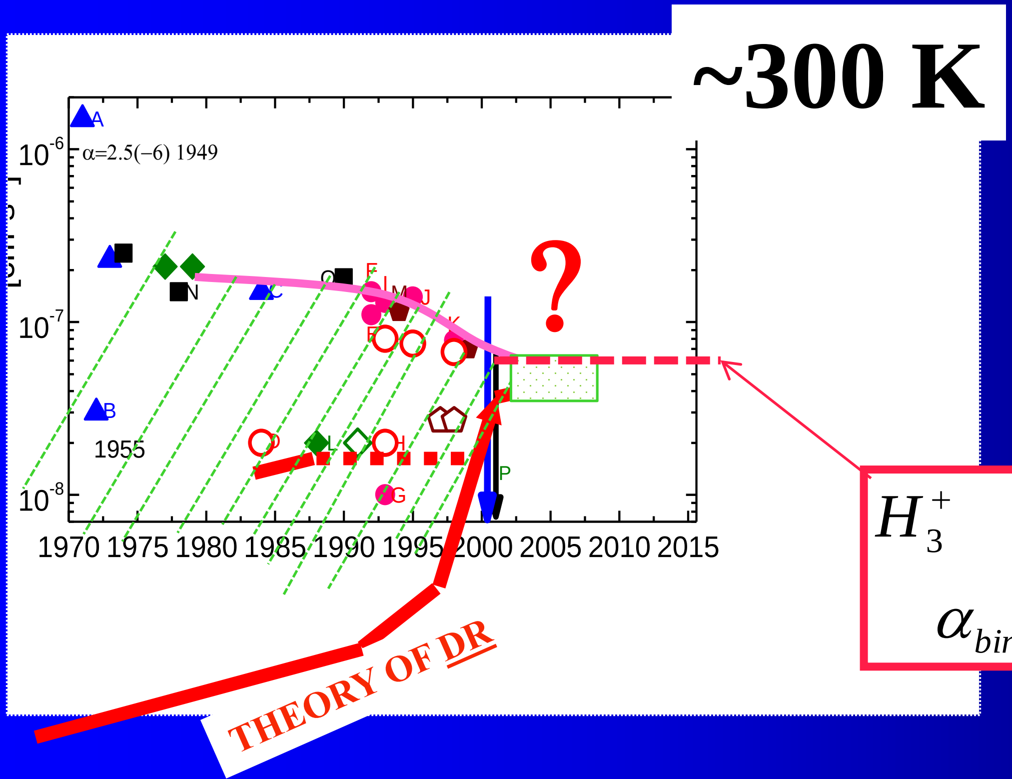



300 K
$H_3^+$
(3,3)
(1,0)
(1,1)
$H_5^+$
$He^m$
$n$ (cm$^{-3}$)
$t$ (µs)

population (%)
Afterglow Discharge
o-$H_3^+$ (3,3)
p-$H_3^+$ (1,1)
o-$H_3^+$ (1,0)
other states
(1,1)
(1,0)
(3,3)
$T_{Rot\text{-}ortho}$ (K)
Discharge
Afterglow
$T_{Kin}$ (K)

# History of experiments –“time evolution“




$H_3^+$ *PLASMA EXPERIMENT*

$$\alpha_{bin}(260K) = 7.5x10^{-8}\,cm^3 s^{-1}$$

**Storage rings** — **TSR CRYRING**

**Afterglow** — **SA FALP**

State selected …2008

$H_3^+$

# Nuclear spin dependence of $H_3^+$ recombination

B. J. McCall, et al. *Physical Review A* (2004)

H. Kreckel, J. Glosik, et al. Phys. Rev. Lett. 2005,

….2008, new improved calculations

Astronomy & Astrophysics
October 13, 2008

L. Pagani[1], C. Vastel[2], E. Hugo[3], V. Kokoouline[4], Chris H. Greene[5], A. Bacmann[6], E. Bayet[7], C. Ceccarelli[6], R. Peng[8], and S. Schlemmer[3]

M. Larsson, B.J. McCall, A.E. Orel (2008)

J. Glosik, R. Plasil, et al. *Phys. Rev. A*, 2009.

H. Kreckel, O. Novotny, et al., Phys. Rev. A（2010）.

K. N. Crabtree, N. Indriolo, et al., Astrophys. J. (2011)

J. Varju, M. Hejduk, J. Glosik, et al. *Phys. Rev. Lett.*, 2011.

P. Dohnal, M. Hejduk, J. Glosik, et al. *J. Chem. Phys.*, 2012.

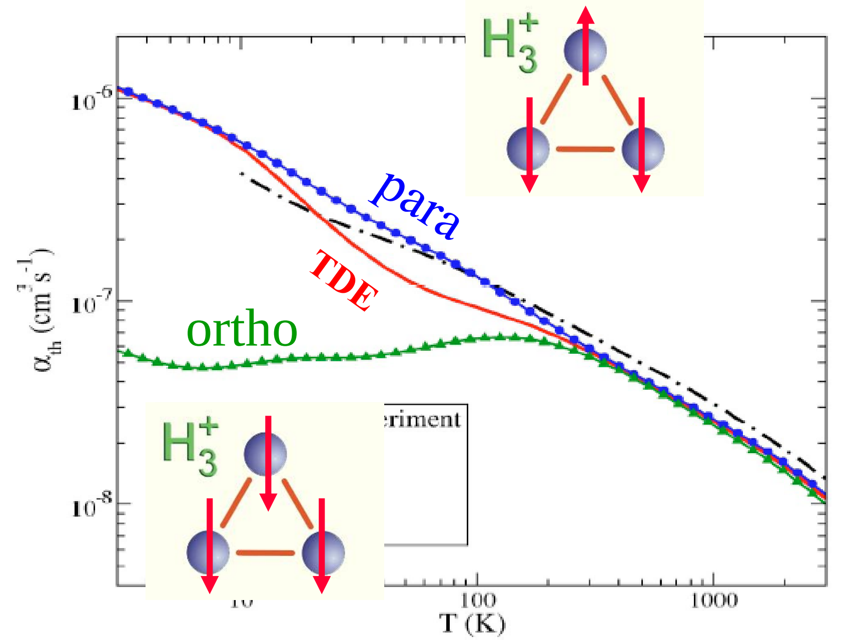



FIG. 5. (Color online) The present theoretical thermal rate coefficient for dissociative recombination of $H_3^+$ is compared with the experimental rate coefficient deduced from the storage ring experiment of McCall and co-workers (Refs. 9 and 10).

**Doubts 2011**

**“Presently no rate coefficient measurement with a confirmed temperature below 300 K exists“.**

**Petrignani *et al.* Phys. Rev. A (2011)**

**. Unfortunately the experiments on storage rings were stopped …. ☹ … ☹…**

**3D 60 K**

# State of the art in 2013???

**The dissociative recombination of $H_3^+$ – a saga coming to an end?**

'Yes, the saga is coming to an end; but slowly.'

M. Larsson, B.J. McCall, A.E. Orel (2008)

**….. Presently no reliable recombination rate coefficient for H3+ measured with storage rings below 300 K exists. …..**

H. Kreckel, O. Novotny, K. N. Crabtree, et al., Phys. Rev. A (2010).
A. Petrignani, S. Altevogt, M. H. Berg, et al., Phys. Rev. A (2011).

The recent observations made towards several diffuse molecular clouds showed large difference between excitation temperatures T10(H2) and T(H3+), for details see ref. [cra11].

These observations lead to conclusion that in reliable chemical models the nuclear spin dependences of the reactions, including recombination of para- and ortho-H3+, have to be considered.
The dependences on spin, rotational excitation and temperature have to be measured.

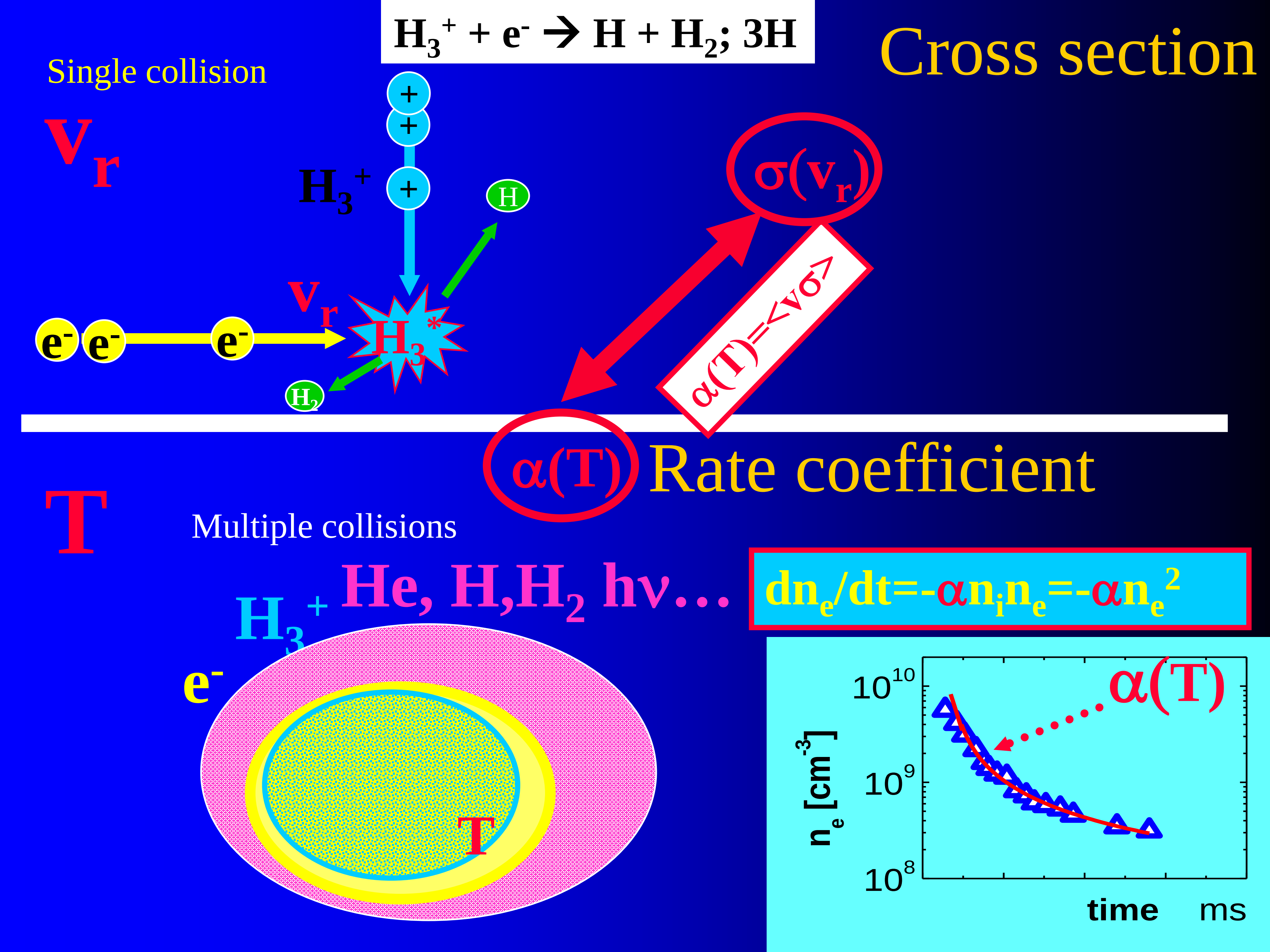
K. N. Crabtree, N. Indriolo, H. Kreckel, B. A. Tom, and B. J. McCall, Astrophys. J. (2011)


**Help! Theory for $H_3^+$ Recombination Still Needed**
**…. *We still badly need theory* …**

**Takeshi Oka, DR2013**

…. It is time to present some recent results from afterglow experiments …

**SA a FALP**



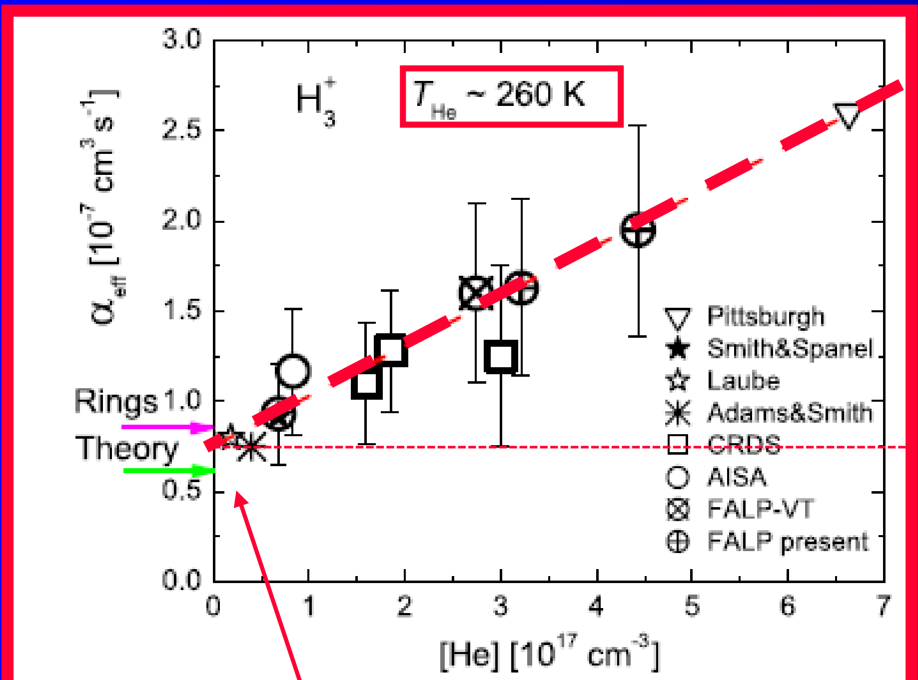
$H_3^+ + e^- \rightarrow H + H_2$; 3H
Cross section
Single collision
$v_r$
$H_3^+$
H
$v_r$
$H_3^*$
$e^-$ $e^-$ $e^-$
$H_2$
$\sigma(v_r)$
$\alpha(T)=<v\sigma>$
$\alpha(T)$ Rate coefficient
T
Multiple collisions
He, H, $H_2$ hν…
$dn_e/dt=-\alpha n_i n_e=-\alpha n_e^2$
$H_3^+$
$e^-$
T
$10^{10}$
$10^9$
$10^8$
$n_e$ [$cm^{-3}$]
time ms
$\alpha(T)$

# DR2007 - Dependence on He and $H_2$ pressure at 260 K

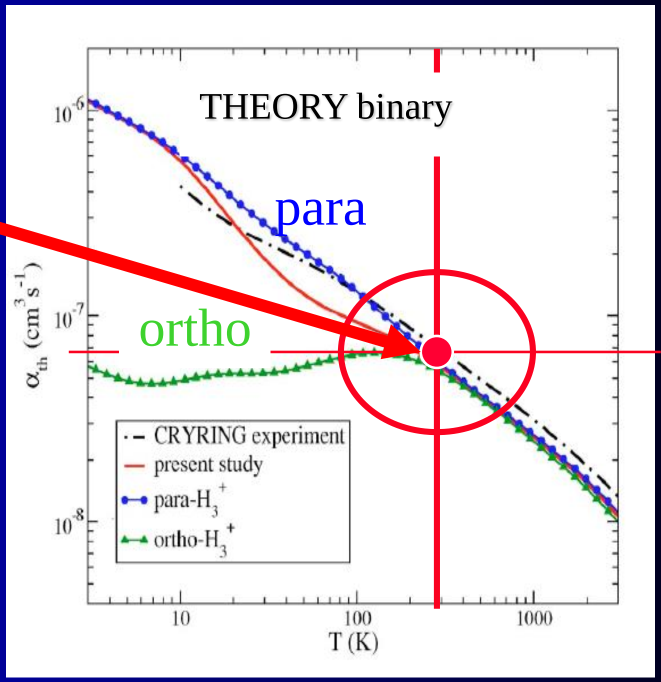
Afterglow in He/Ar/$H_2$ mixture

$a_{eff} = a_{eff}(T_e, T_i, n_e, [He], [H_2], {}^{o/p}f_2, {}^{o/p}f_3)$

$a_{eff} = a_{eff}(T, [He])$




$$\alpha_{eff} = \alpha_{bin} + K_{He}.[He]$$



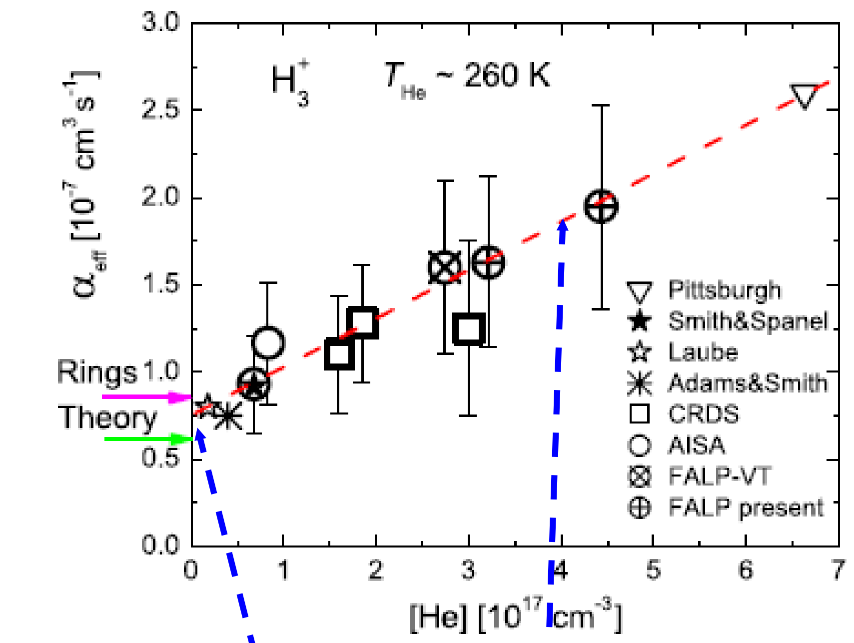

$$H_3^+ + e \overset{\alpha^*}{\rightleftarrows} H_3^* \rightarrow products$$

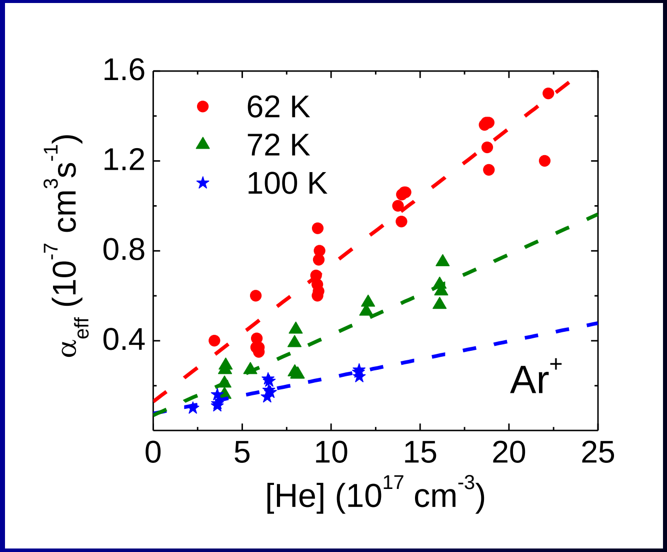
He,

J. Phys. B: At. Mol. Opt. Phys. 41 (2008) 191001 (6pp)

Battle ships

# Binary + He assisted ternary recombination




$$\alpha_{eff} = \alpha_{bin} + K_{He}.[He]$$

$$H_3^+ + e^- \xrightarrow{\alpha_{Bin}} H_2 + H,.H + H + H$$

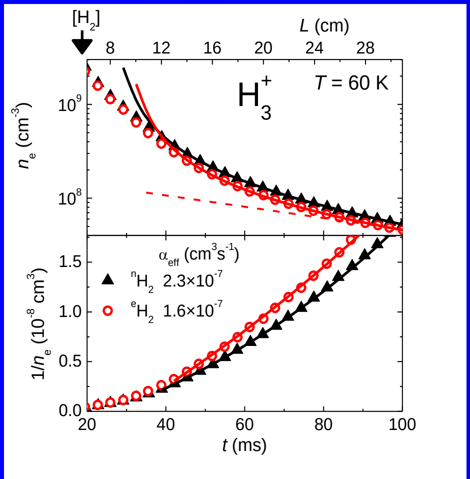
$$H_3^+ + e^- \underset{\tau a}{\overset{\alpha_F}{\rightleftarrows}} H_3^{\#} \xrightarrow[+He\ldots ks_{He}]{} \text{neutrals}$$

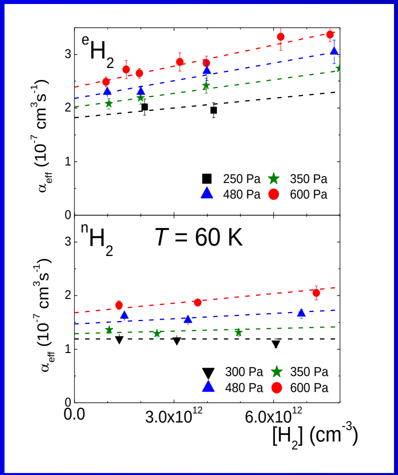
$$H_3^+ \quad PLASMA\ \ EXPERIMENT \quad \alpha_{bin}(260K) = 7.5x10^{-8}\,cm^3 s^{-1}$$

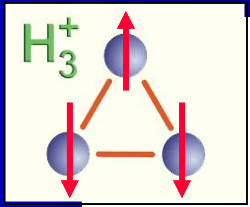
J. Phys. B: At. Mol. Opt. Phys. 41 (2008) 191001 (6pp)

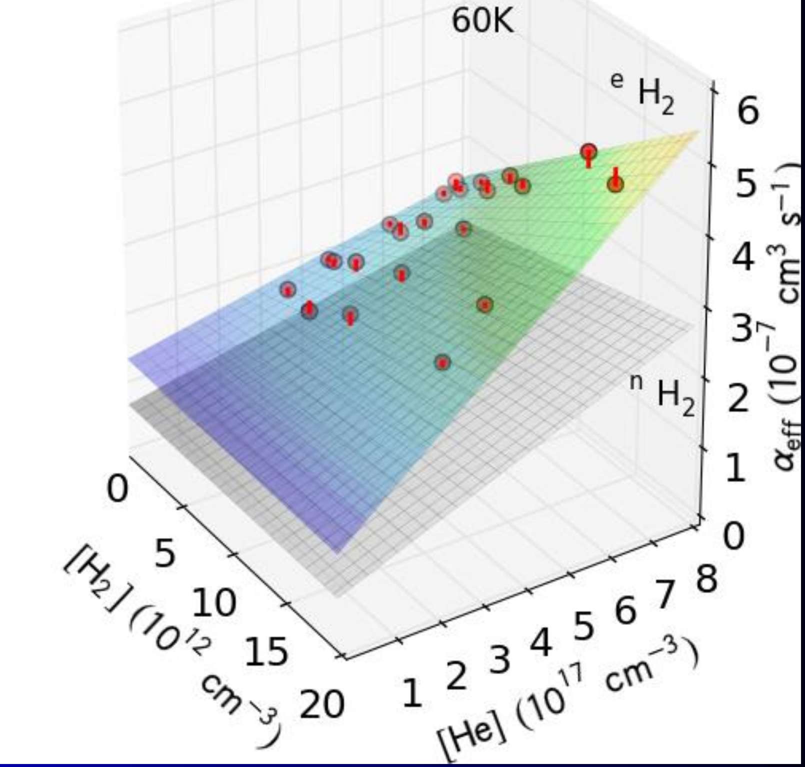
Just before splitting ☺

$$\alpha_{eff} = \alpha_{eff}(T_e, T_i, n_e, [He], [H_2], {}^{o/p}f_3)$$

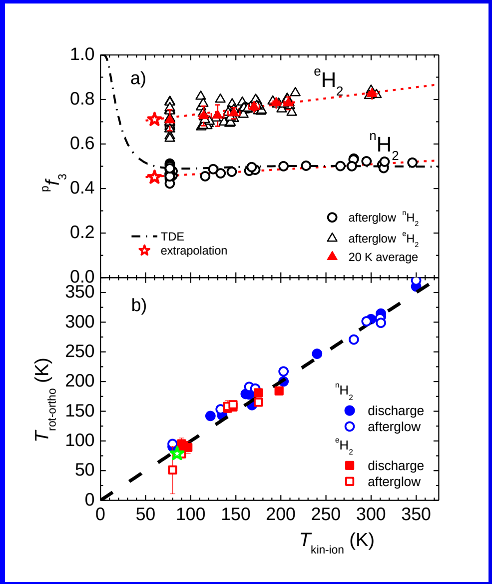


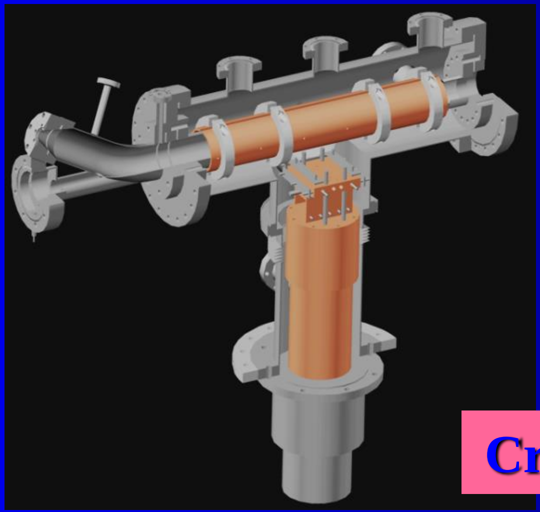




$$T = T_{wall} = T_{He} = T_e = T_{rot} = T_{kin\text{-}ion}$$



**Cryo-FALP II**

model

# Model

**$\alpha_{eff} = \alpha_{eff}(T_e, T_i, n_e, [He], [H_2], {}^{o/p}f_3)$**

$$H_3^+ + e^- \xrightarrow{\alpha_{Bin}} H_2 + H, H + H + H$$

$$] \quad \underset{\tau a}{\overset{\alpha_F}{\rightleftarrows}} H_3^\# \xrightarrow[He \ldots ks_{He}]{H_2 \ldots ks_{H2}} \text{neutrals}$$

**By solving the set of balance equations we obtain:**

(He/Ar/$H_2$ mixture)

$$\frac{\partial n_e}{\partial t} = -(\alpha_{bin} - \alpha_F \frac{k_{SHe}[He] + k_{SH_2}[H_2]}{\frac{1}{\tau_a} + k_{SHe}[He] + k_{SH_2}[H_2]})[H_3^+]n_e$$

$$K_{He} = \alpha_F k_{SHe} \tau_a \qquad K_{H2} = \alpha_F k_{SH2} \tau_a$$

$$\alpha_{eff} = \alpha_{bin} + \alpha_F \frac{K_{He}[He] + K_{H2}[H_2]}{\alpha_F + K_{He}[He] + K_{H2}[H_2]}$$

**In the low density limit ([He] and $[H_2] \rightarrow 0$), linear approximation**

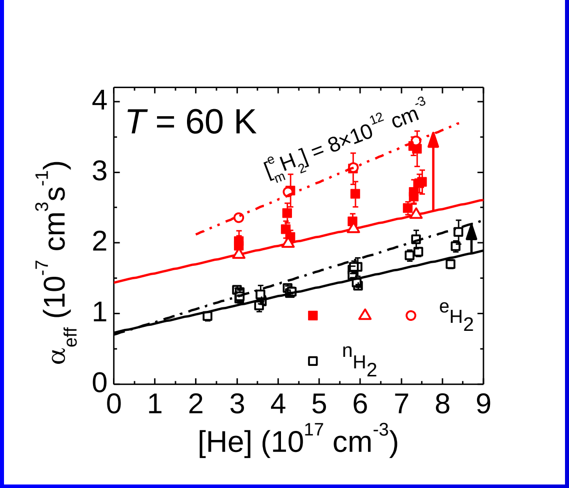
$$\alpha_{eff} = \alpha_{bin} + K_{He}[He] + K_{H2}[H_2]$$

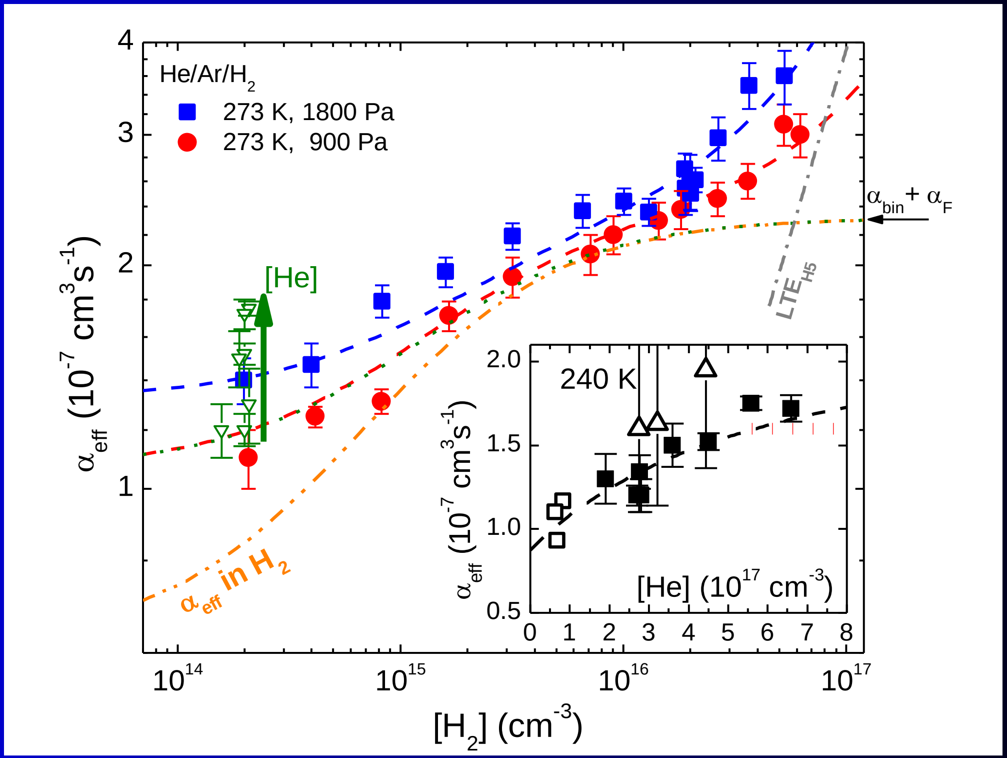
# Experiments - State of the art in 2015

$$H_3^+ + e + He \rightarrow \ldots\ldots + He$$

$$H_3^+ + e + H_2 \rightarrow \ldots\ldots + H_2$$

$$H_3^+ + e + He \rightarrow \ldots\ldots + He$$




$$\alpha_{\mathrm{eff}} = \alpha_{\mathrm{bin}} + \alpha_{\mathrm{F}} \frac{K_{\mathrm{He}}[\mathrm{He}] + K_{\mathrm{H2}}[\mathrm{H_2}]}{\alpha_{\mathrm{F}} + K_{\mathrm{He}}[\mathrm{He}] + K_{\mathrm{H2}}[\mathrm{H_2}]}$$

## CRR

$$H_3^+ + e + e \rightarrow \ldots\ldots + e$$

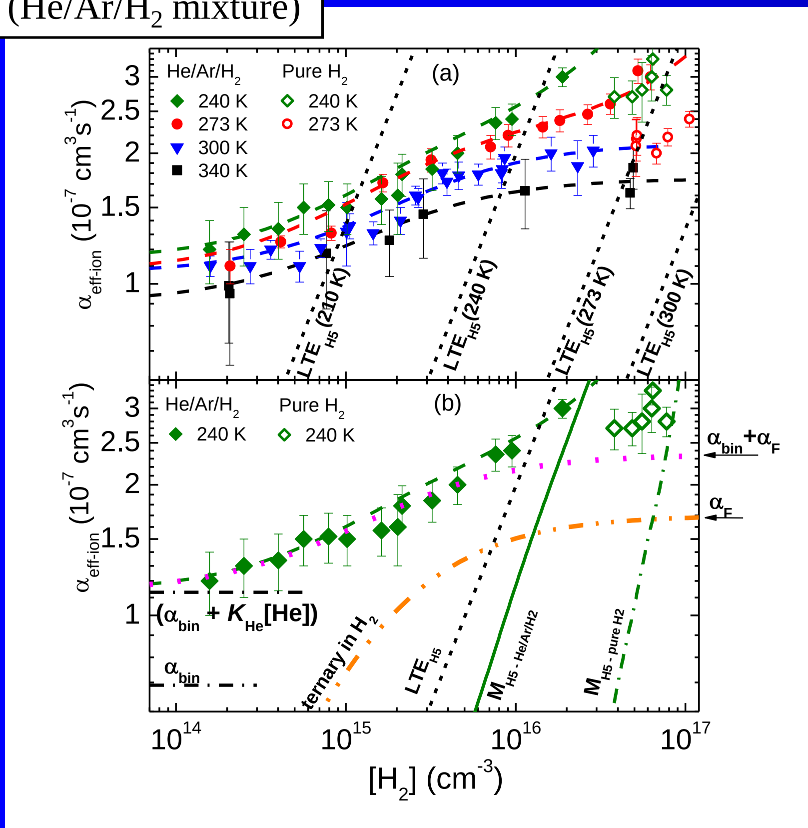
Rate coefficient binary

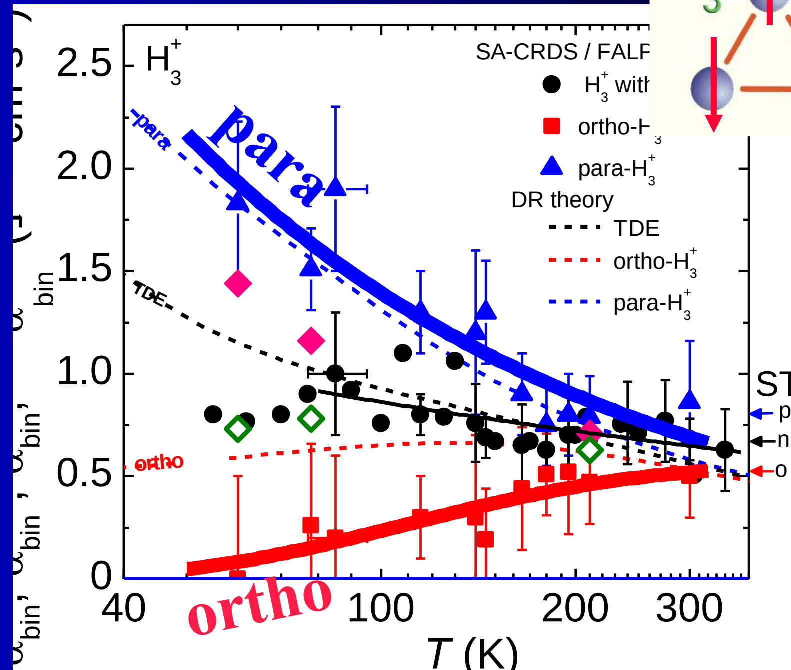
## para-$H_3^+$ and orto-$H_3^+$

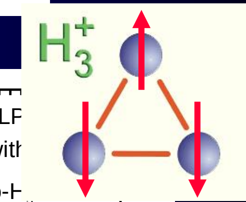
$$H_3^+ + e^- \xrightarrow{\alpha_{Bin}} H_2 + H, H + H + H$$

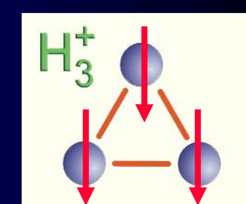
$$H_3^+ + e^- \underset{\tau a}{\overset{\alpha_F}{\rightleftarrows}} H_3^{\#} \xrightarrow[He....ks_{He}]{H_2....ks_{H2}} \text{neutrals}$$

(He/Ar/$H_2$ mixture)



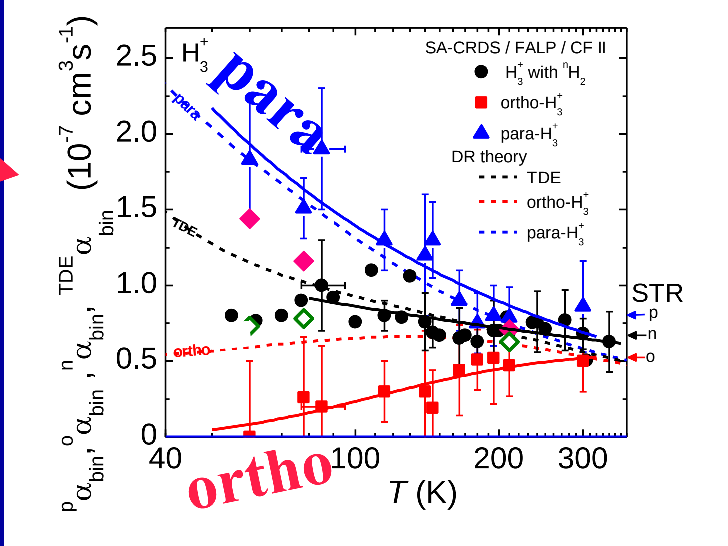



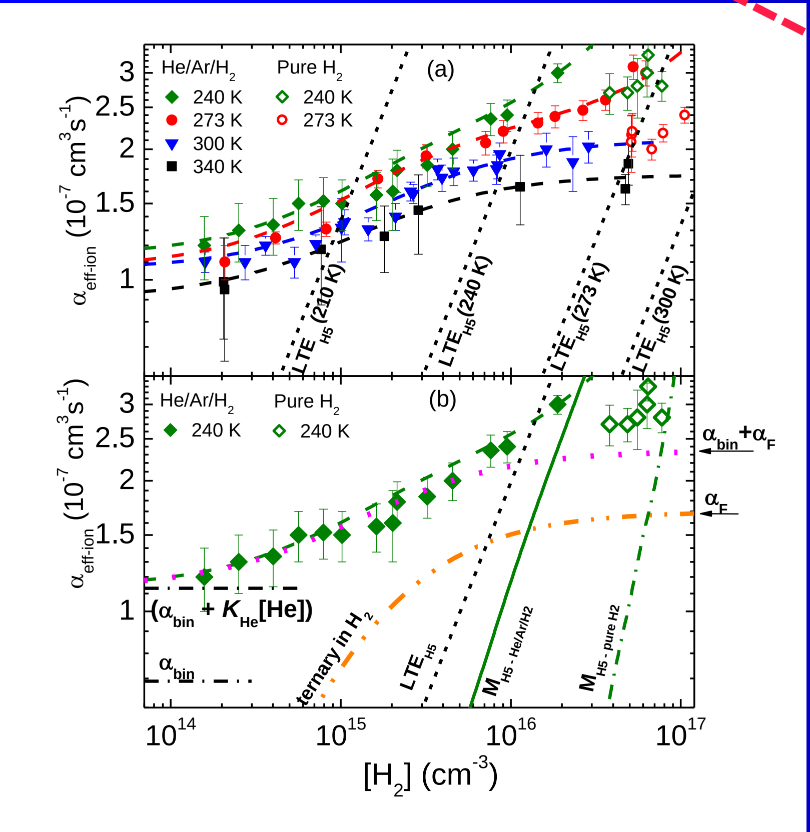



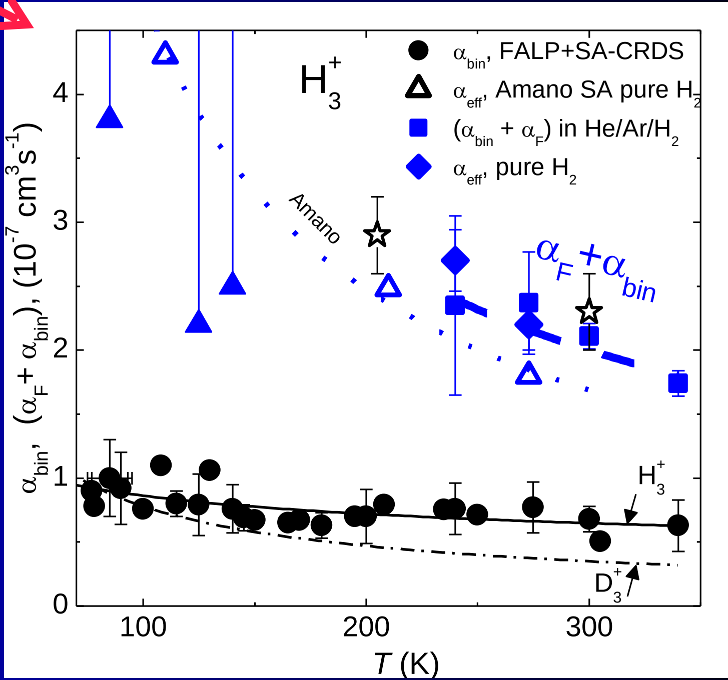
$$H_3^+ + e^- \xrightarrow{\alpha_{Bin}} H_2 + H, H + H + H$$

$$H_3^+ + e^- \underset{\tau_a}{\overset{\alpha_F}{\rightleftarrows}} H_3^\# \underset{He \ldots ks_{He}}{\overset{H_2 \ldots ks_{H2}}{\longrightarrow}} \text{neutrals}$$

## para-$H_3^+$ and orto-$H_3^+$



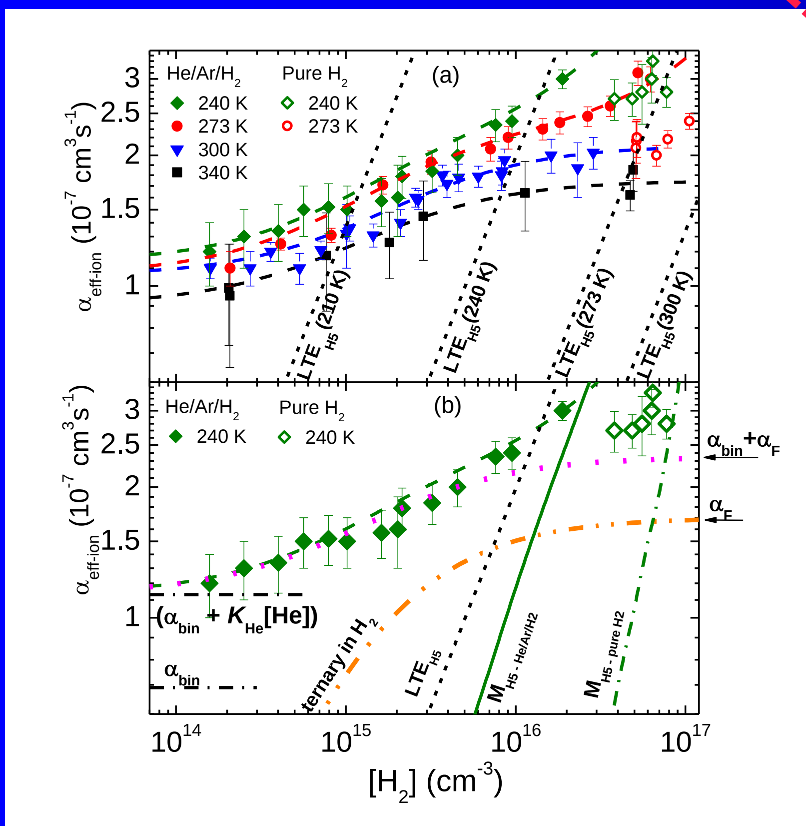
$$H_3^+ + e^- \xrightarrow{\alpha_{Bin}} H_2 + H, H + H + H$$

$$H_3^+ + e^- \underset{\tau_a}{\overset{\alpha_F}{\rightleftarrows}} H_3^{\#} \xrightarrow{H_2 \ldots ks_{H2}} \text{neutrals}$$

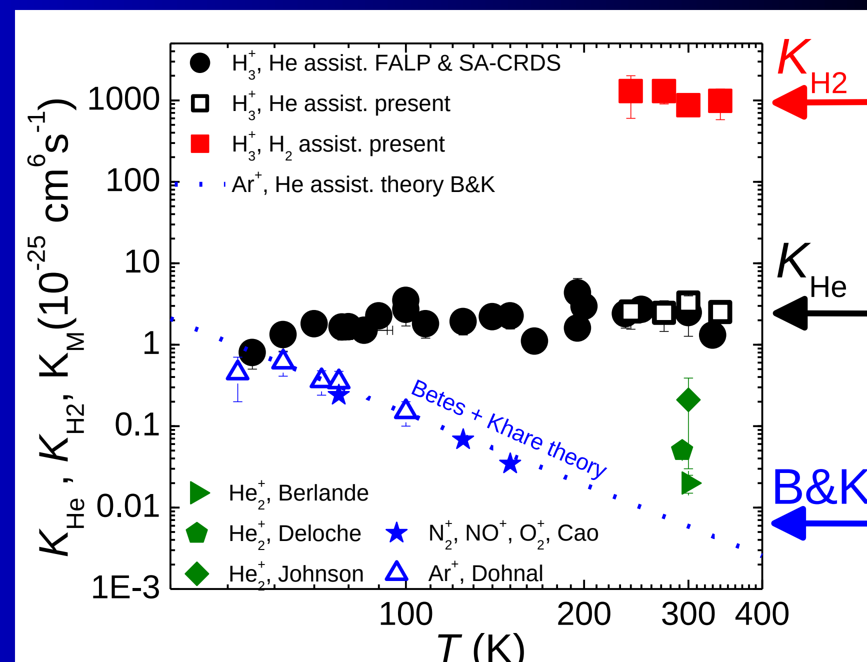
$$H_3^{\#} \xrightarrow[He \ldots ks_{He}]{} \text{neutrals}$$

$$K_{He} = \alpha_F \, k_{SHe} \, \tau_a \qquad K_{H2} = \alpha_F \, k_{SH2} \, \tau_a$$

$$\alpha_{eff} = \alpha_{bin} + \alpha_F \frac{K_{He}[He] + K_{H2}[H_2]}{\alpha_F + K_{He}[He] + K_{H2}[H_2]}$$




# $K_{He}$ $K_{H2}$



IOP Publishing Plasma Sources Science and Technology
Plasma Sources Sci. Technol. 24 (2015) 065017 (10pp) doi:10.1088/0963-0252/24/6/065017

# Recombination of $H_3^+$ ions with electrons in He/$H_2$ ambient gas at temperatures from 240 K to 340 K

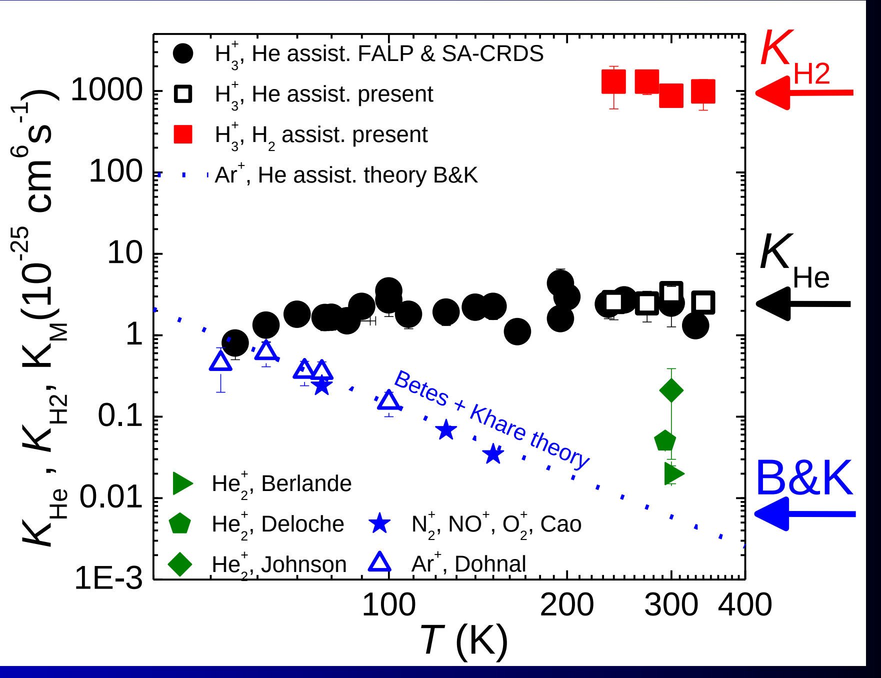
J Glosík[1], P Dohnal[1], P Rubovič[1], Á Kálosi[1], R Plašil[1], Š Roučka[1] and R Johnsen[2]

$$K_{He} = \alpha_F \, k_{SHe} \, \tau_a \qquad K_{H2} = \alpha_F \, k_{SH2} \, \tau_a$$

$$H_3^+ + e + H_2 \rightarrow \ldots\ldots + H_2$$

$$H_3^+ + e + He \rightarrow \ldots\ldots + He$$

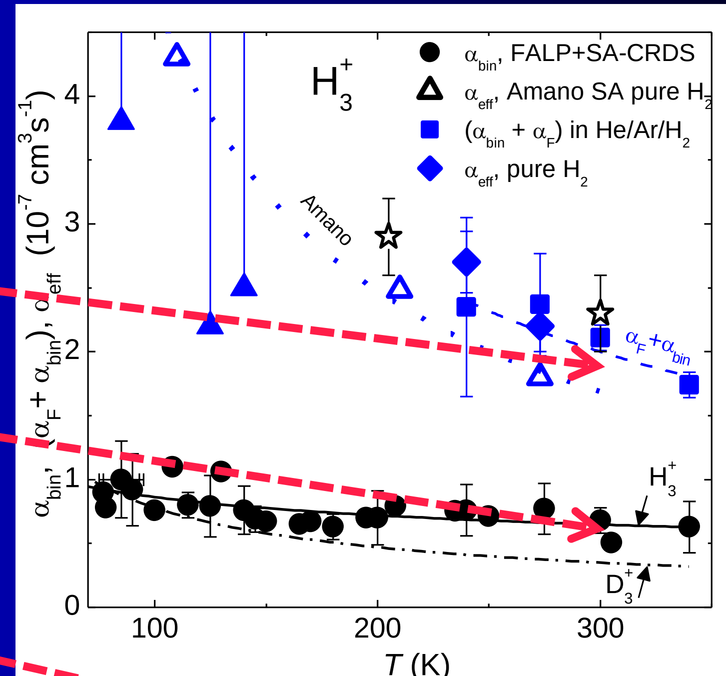
$$Ar^+ + e + He \rightarrow \ldots\ldots + He$$



$H_3^+/e^-$ plasma in He/Ar/$H_2$ gas mixture

$$H_3^+ + e^- \Rightarrow H + H_2, 3H$$

**α(T=300 K)**

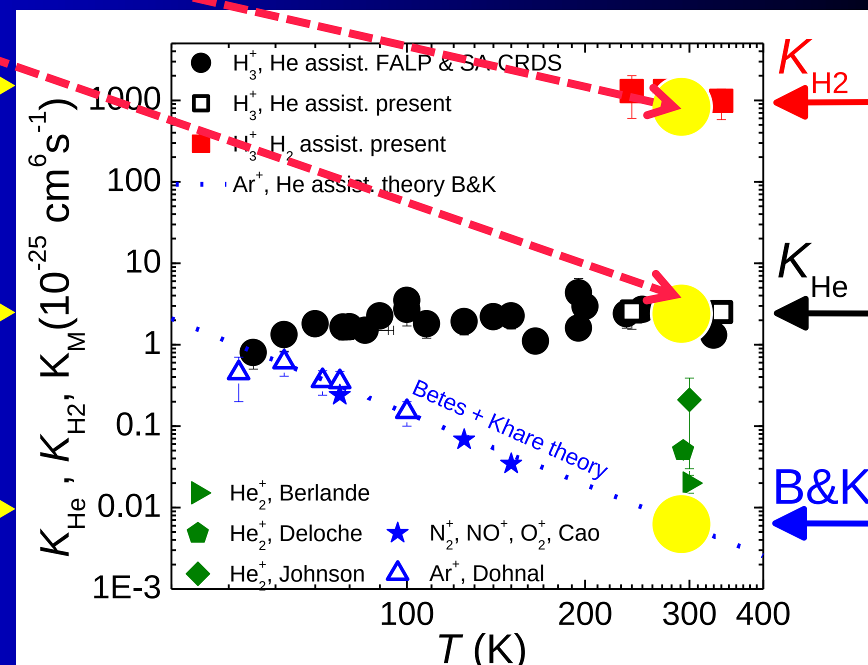


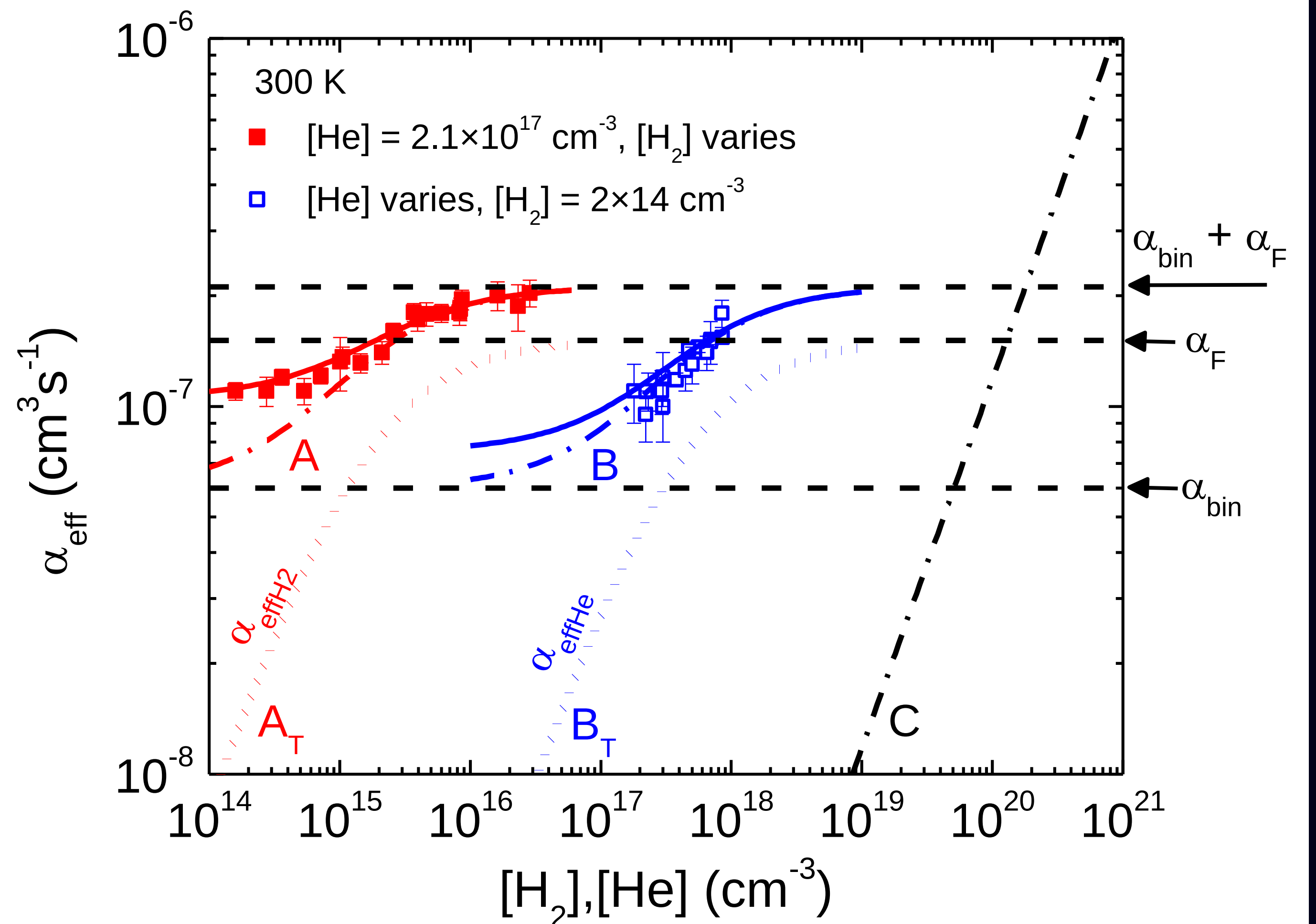

$$\alpha_{eff} = \alpha_{bin} + \alpha_F \frac{K_{He}[He] + K_{H2}[H_2]}{\alpha_F + K_{He}[He] + K_{H2}[H_2]}$$

$$H_3^+ + e + H_2 \rightarrow \ldots\ldots + H_2$$

$$H_3^+ + e + He \rightarrow \ldots\ldots + He$$

$$Ar^+ + e + He \rightarrow \ldots\ldots + He$$





300 K
[He] = 2.1×10^17 cm^-3, [H2] varies
[He] varies, [H2] = 2×14 cm^-3
αbin + αF
αF
αbin
A
B
C
AT
BT
αeffH2
αeffHe
αeff (cm3s-1)
[H2],[He] (cm-3)
10-6
10-7
10-8
1014
1015
1016
1017
1018
1019
1020
1021

# $Ar^+ + e^- + e^-$

# $H^+ + e^- + e^-$

Anti hydrogen formation

Colisional Radiative Recombination -CRR

$$\frac{dn_e}{dt} = -K_{CRR}\ [Ar^+] n_e^2 - \frac{n_e}{\tau_D} = -K_{CRR}\ n_e^3 - \frac{n_e}{\tau_D}$$

$$\alpha_{CRR} = K_{CRR}\ n_e$$

# Kvantovka na každý deň

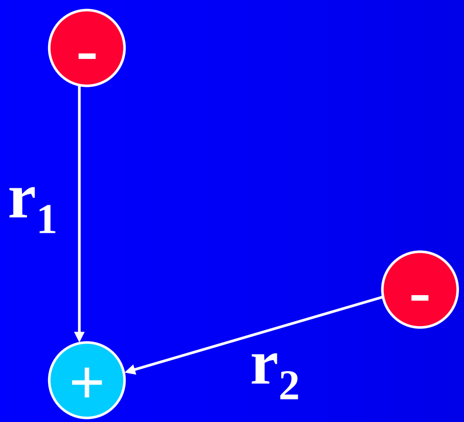
## $H^+ + e^- + e^- \rightarrow H + e^-$

PRL **98,** 133201 (2007) PHYSICAL REVIEW LETTERS week ending 30 MARCH 2007

**Three-Body Recombination of Atomic Ions with Slow Electrons**

S. X. Hu

*Laboratory for Laser Energetics, University of Rochester, 250 East River Road, Rochester, New York 14623, USA*





We consider the simplest TBR in the case of hydrogen formation, in which two free electrons interact with a proton. To investigate the three-body interaction dynamics, we numerically solve the six-dimensional (6D) time-dependent Schrödinger equation, which has the following form (atomic units are used throughout):

$$i\frac{\partial}{\partial t}\Phi(\mathbf{r}_1, \mathbf{r}_2, t) = \left[-\frac{1}{2}(\Delta_{\mathbf{r}_1} + \Delta_{\mathbf{r}_2}) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right]\Phi(\mathbf{r}_1, \mathbf{r}_2, t), \quad (1)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of each electron, with respect to the proton. We obtain a more tractable

with respect to the proton. We obtain a more tractable solution by using the close-coupling recipe [12]: expanding the 6D wave function $\Phi(\mathbf{r}_1, \mathbf{r}_2|t)$ in terms of bipolar spherical harmonics $Y_{l_1 l_2}^{LS}(\Omega_1, \Omega_2)$, $\Phi(\mathbf{r}_1, \mathbf{r}_2|t) = \sum_{LS}\sum_{l_1 l_2}[\Psi_{l_1 l_2}^{(LS)}(r_1, r_2|t)/r_1 r_2]Y_{l_1 l_2}^{LS}(\Omega_1, \Omega_2)$, for a specific symmetry ($LS$). We can also expand the Coulomb repulsion term $1/|\mathbf{r}_1 - \mathbf{r}_2|$ in terms of spherical harmonics. Substituting these expansions into the above Schrödinger Eq. (1) and integrating over the angles $\Omega_1$ and $\Omega_2$ yields a set of coupled partial differential equations with only two radial variables $r_1$ and $r_2$ left:

$$i\frac{\partial}{\partial t}\Psi_j(r_1, r_2|t) = [\hat{T}_1 + \hat{T}_2 + \hat{V}_c]\Psi_j(r_1, r_2|t) + \sum_k \hat{V}_{j,k}^I(r_1, r_2|t)\Psi_k(r_1, r_2|t), \quad (2)$$

where the partial-wave index $j$ runs from 1 to the total number $N$ of partial waves used for expansion. In Eq. (2),

# Kvantovka na každý deň

$$i\frac{\partial}{\partial t}\Psi_j(r_1, r_2|t) = [\hat{T}_1 + \hat{T}_2 + \hat{V}_c]\Psi_j(r_1, r_2|t) + \sum_k \hat{V}^I_{j,k}(r_1, r_2|t)\Psi_k(r_1, r_2|t), \qquad (2)$$

## $H^+ + e^- + e^- \rightarrow H + e^-$

$$P_{nl}(E_2) = 2\sum_{LS}\sum_{l_2}\left|\int dr_1 \int dr_2 \phi^*_{nl}(r_1)\phi^*_{k_2 l_2}(r_2)\Psi^{(LS)}_{ll_2}(r_1, r_2, t = t_f)\right|^2,$$

## $K_E$=0.1 eV

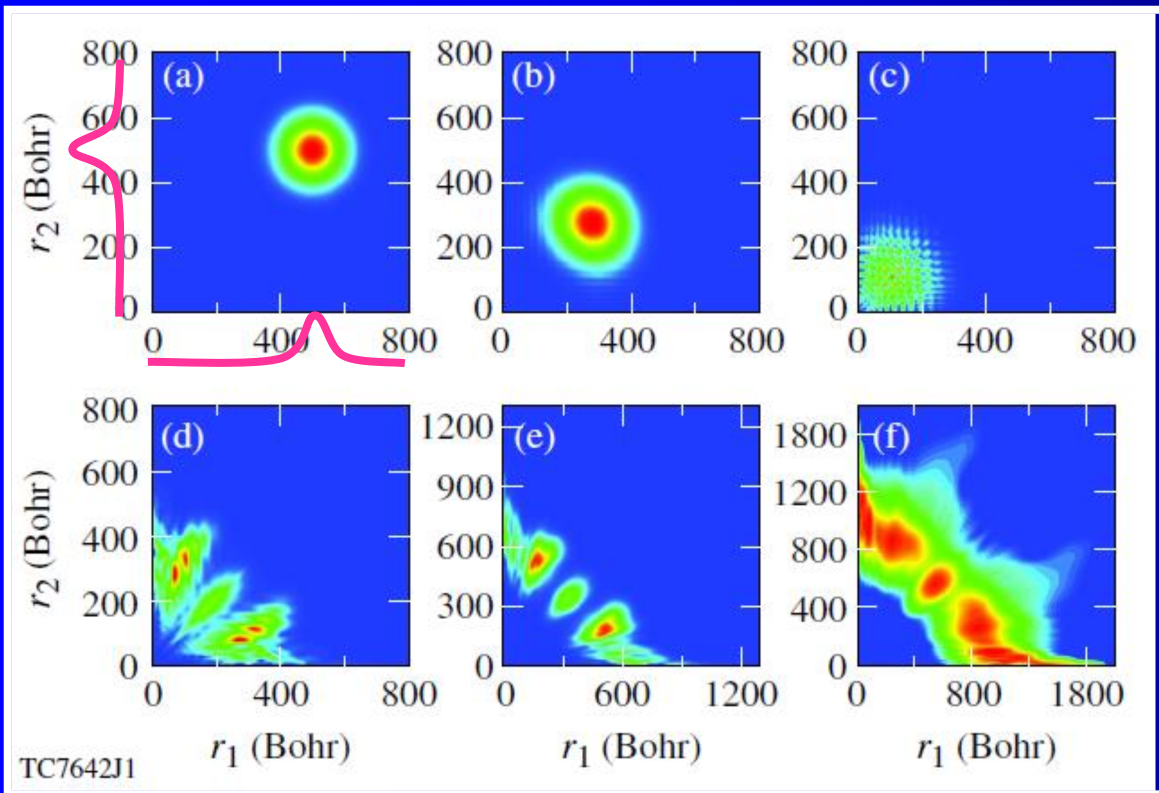
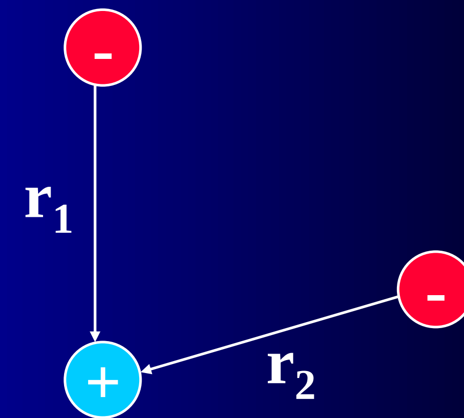
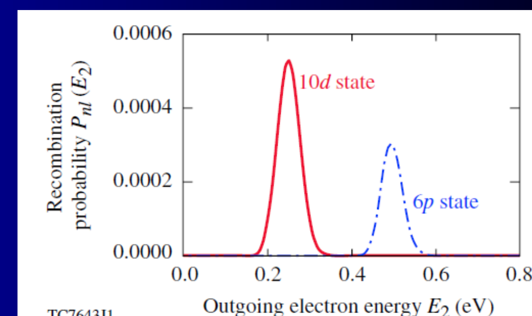



FIG. 1 (color online). Snapshots of electron probability distribution on the plane spanned by the radial coordinates $r_1$ and $r_2$ for different times: (a) $t = 0.0$ fs, (b) $t = 60$ fs, (c) $t = 100$ fs, (d) $t = 150$ fs, (e) $t = 194$ fs, and (f) (in log scale) $t = 260$ fs.




Thus, for the case of $K_E = 0.1$ eV considered in Figs. 1 and 2, the total system energy is about $E_{tot} \sim 0.12$ eV instead of $2K_E$. Hence, when one electron recombines to the 10$d$ state ($|E_{10d}| \approx 0.136$ eV) of the H atom, the outgoing electron takes an initial total energy of 0.12 eV plus $|E_{10d}|$, thereby $P_{10d}(E_2)$ peaks at $E_2 \sim 0.256$ eV, as shown by the (red) solid line of Fig. 2. Similar energy conservation is also well satisfied for the recombination to the 6$p$ state, as is illustrated by the (blue) dash-dotted line in Fig. 2. Our quantum calculations unambiguously reveal the essential feature of a TBR process.

# Kvantovka na každý deň

$H^+ + e^- + e^- \rightarrow H + e^-$

$K_E = 0.1$ eV

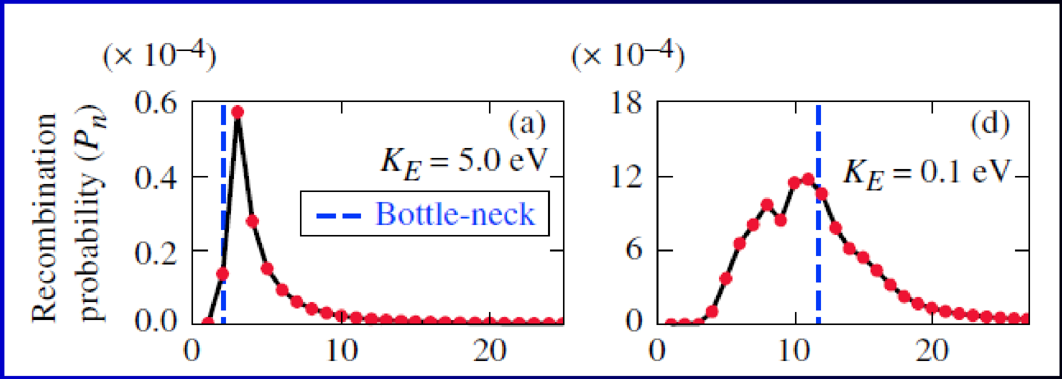
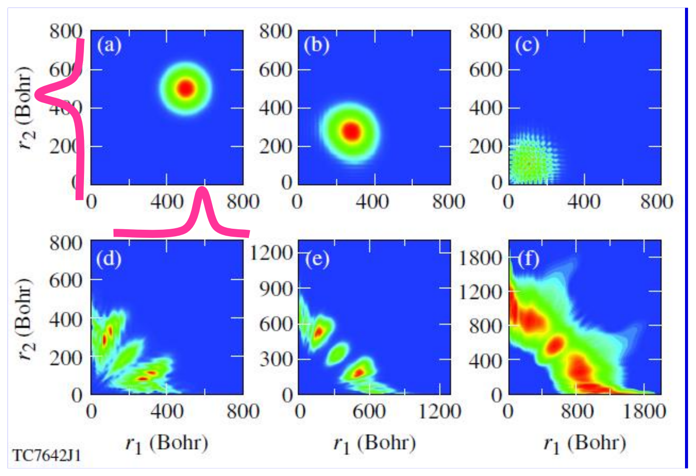
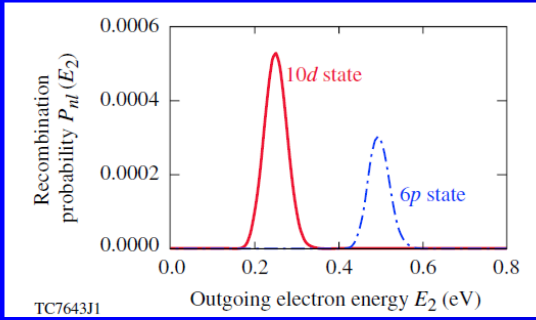



FIG. 3 (color online). The recombination probability $P_n$ as a function of the energy level $n$, for different electron kinetic energies $K_E$ marked in each panel.



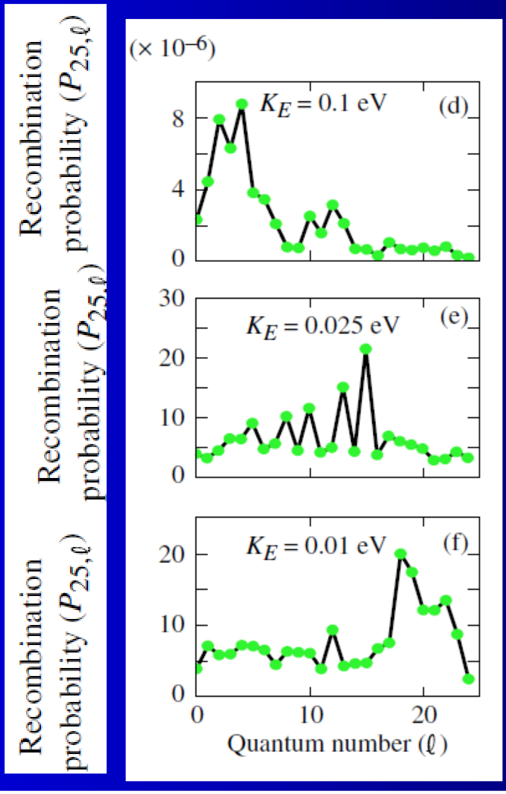




FIG. 4 (color online). The recombination probability $P_{n=25,l}$ as a function of the angular-momentum quantum number $l$, for different electron kinetic energies $K_E$ marked in each panel.

# $Ar^+ + e^- + e^-$

# $H^+ + e^- + e^-$

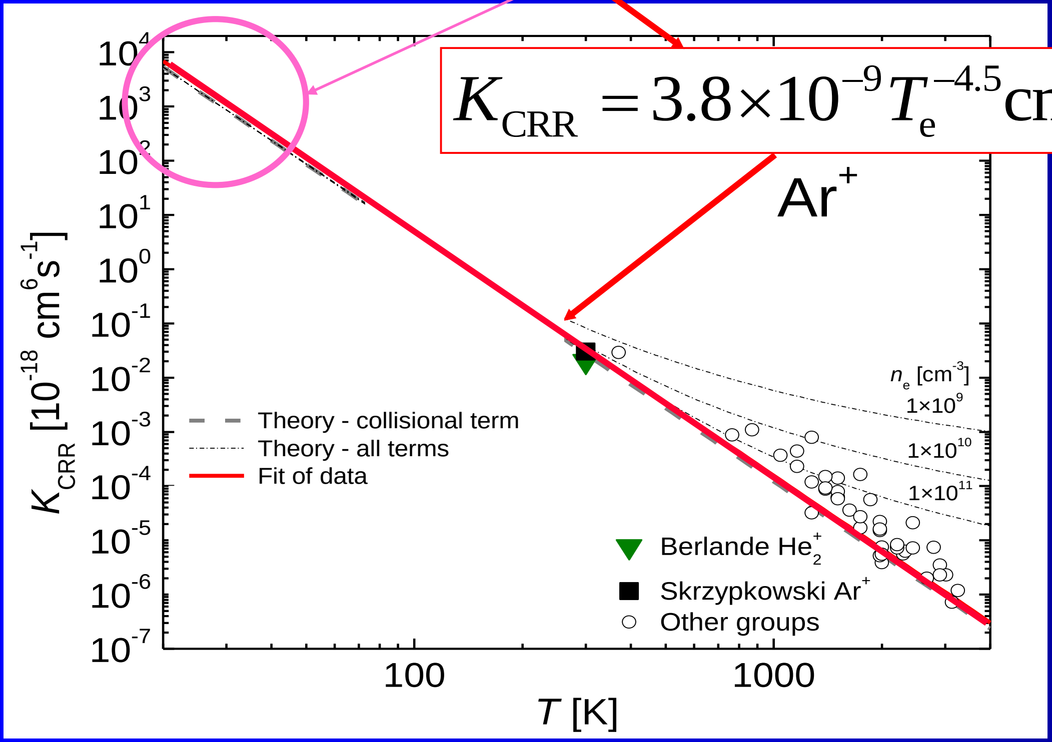
Anti hydrogen formation

$$\frac{dn_e}{dt} = -K_{CRR}\,[Ar^+]\,n_e^2 - \frac{n_e}{\tau_D} = -K_{CRR}\,n_e^3 - \frac{n_e}{\tau_D}$$

$$\alpha_{\mathrm{CRR}} = 3.8\times10^{-9}T_e^{-4.5}n_e + 1.55\times10^{-10}T_e^{-0.63} + 6\times10^{-9}T_e^{-2.18}n_e^{0.37}\,\mathrm{cm}^3\mathrm{s}^{-1}$$

$$\alpha_{CRR} = K_{CRR}\,n_e$$

$$K_{\mathrm{CRR}} = 3.8\times10^{-9}T_e^{-4.5}\,\mathrm{cm}^6\mathrm{s}^{-1}$$

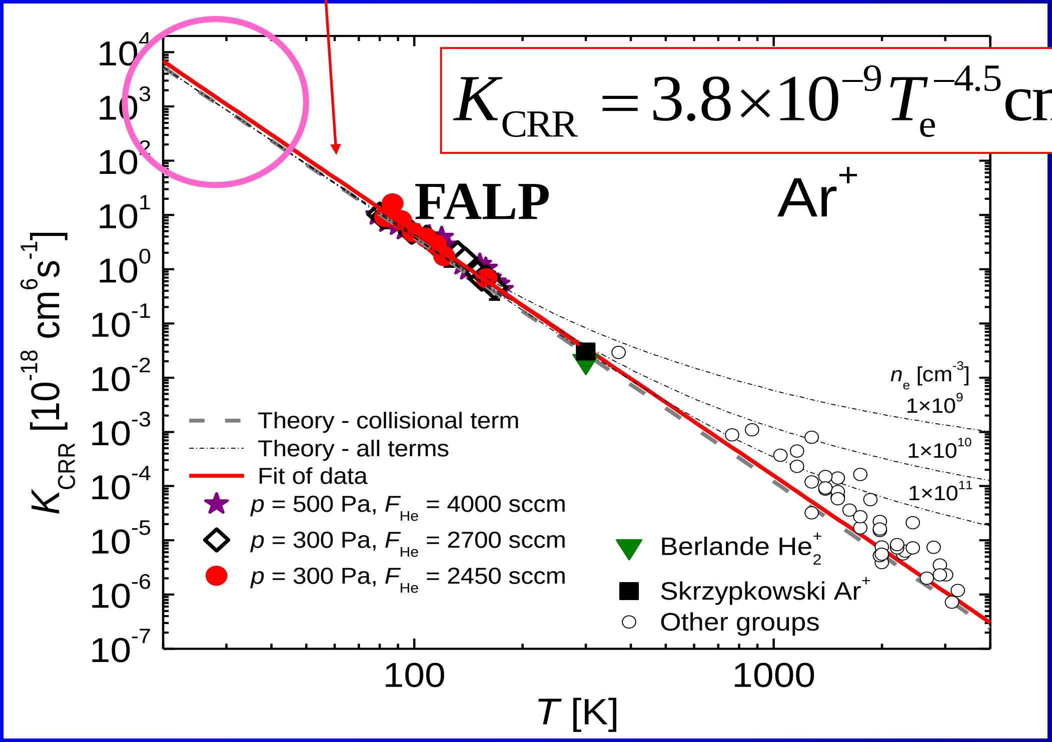


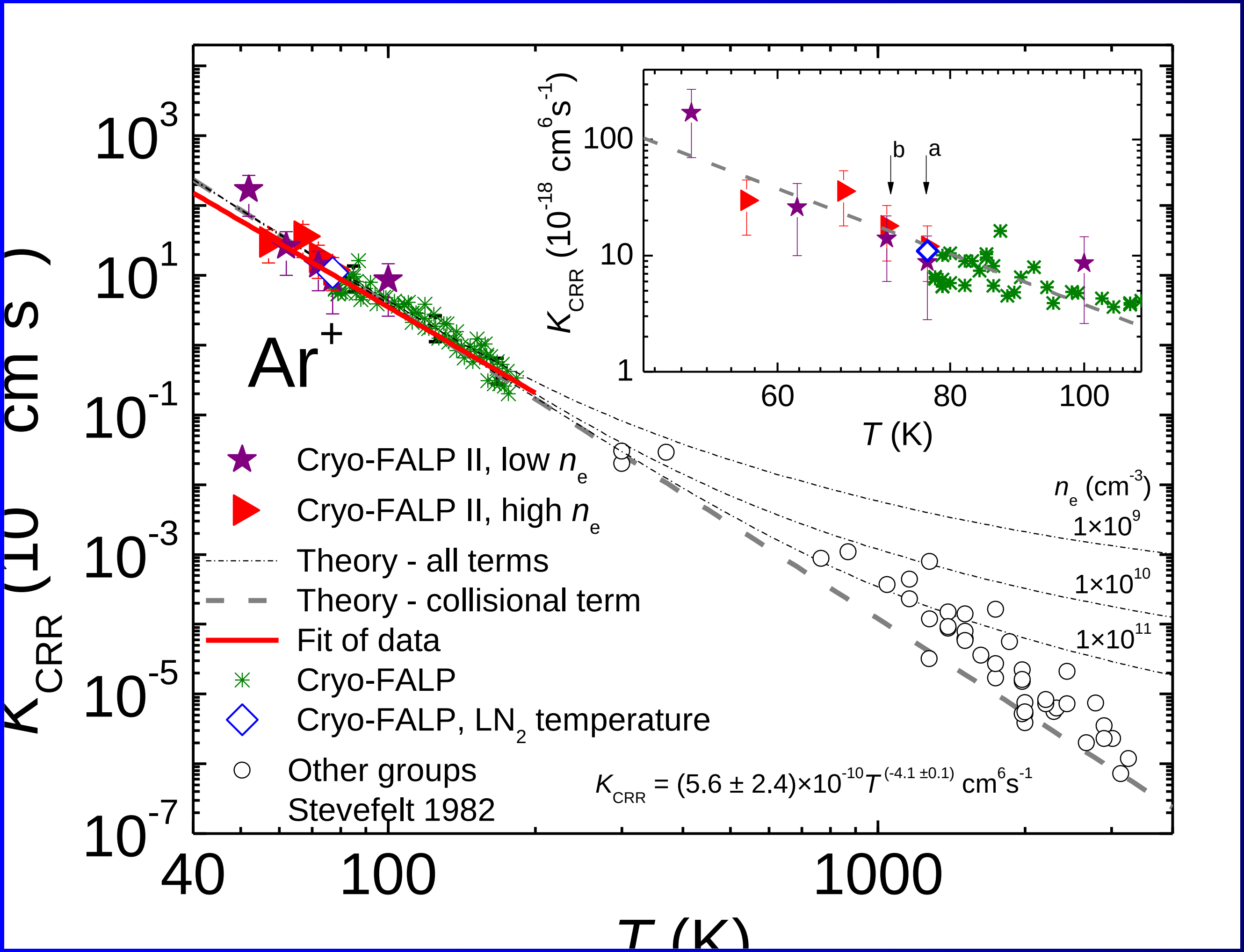
# $Ar^+ + e^- + e^-$

$$\frac{dn_e}{dt} = -K_{CRR}\,[Ar^+]n_e^2 - \frac{n_e}{\tau_D} = -K_{CRR}\,n_e^3 - \frac{n_e}{\tau_D}$$

$$\alpha_{\mathrm{CRR}} = 3.8\times10^{-9}T_{\mathrm{e}}^{-4.5}n_{\mathrm{e}} + 1.55\times10^{-10}T_{\mathrm{e}}^{-0.63} + 6\times10^{-9}T_{\mathrm{e}}^{-2.18}n_{\mathrm{e}}^{0.37}\mathrm{cm^3s^{-1}}$$

$$K_{\mathrm{CRR}} = 3.8\times10^{-9}T_{\mathrm{e}}^{-4.5}\mathrm{cm^6s^{-1}}$$



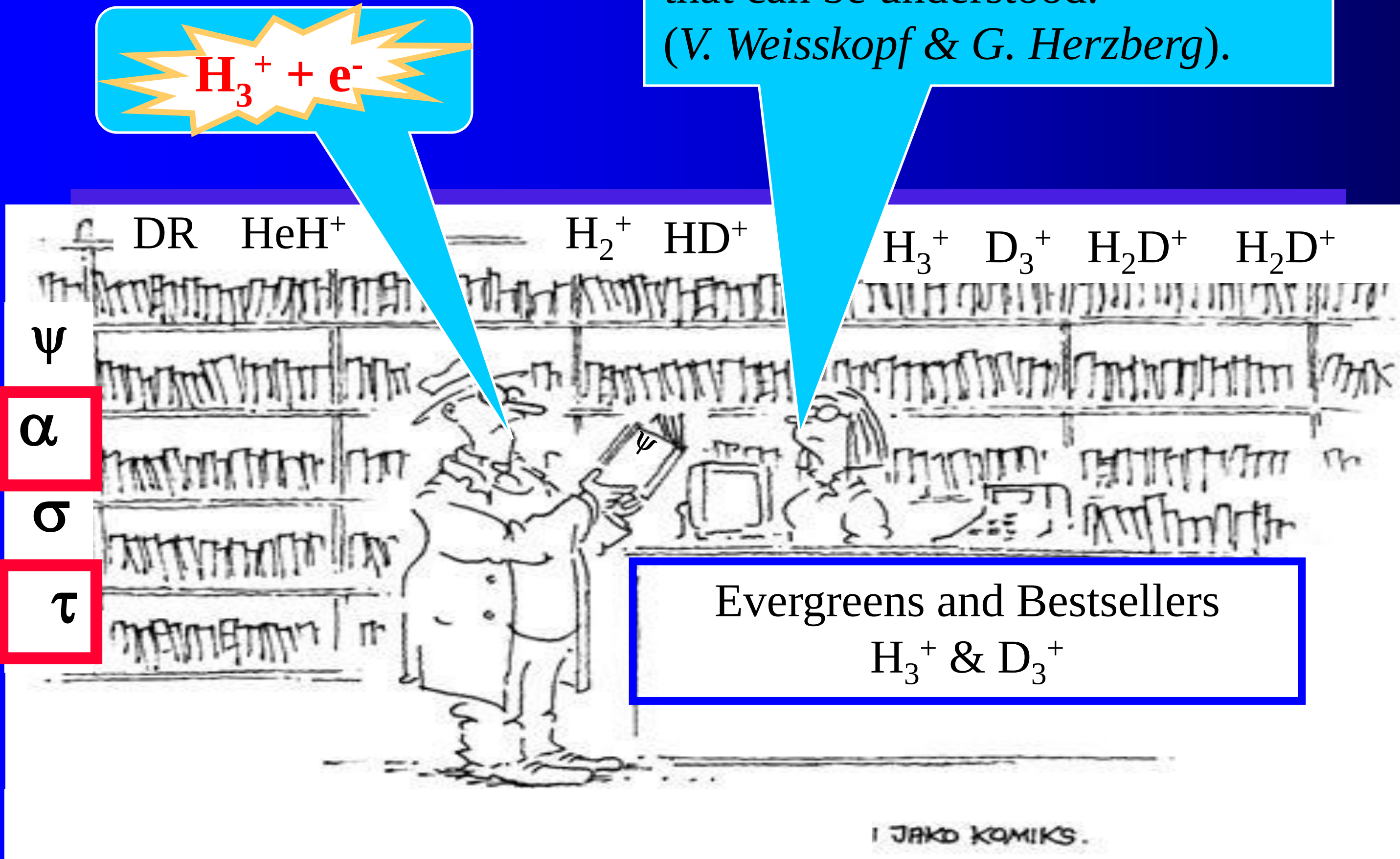


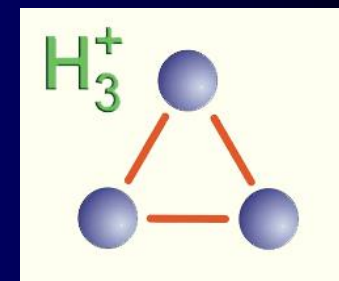
Ar+
Cryo-FALP II, low $n_e$
Cryo-FALP II, high $n_e$
Theory - all terms
Theory - collisional term
Fit of data
Cryo-FALP
Cryo-FALP, $LN_2$ temperature
Other groups
Stevefelt 1982
$n_e$ (cm$^{-3}$)
1×10$^9$
1×10$^{10}$
1×10$^{11}$
$K_{CRR} = (5.6 \pm 2.4)\times10^{-10} T^{(-4.1 \pm 0.1)}$ cm$^6$s$^{-1}$
$K_{CRR}$ (10$^{-18}$ cm$^6$s$^{-1}$)
T (K)
b
a

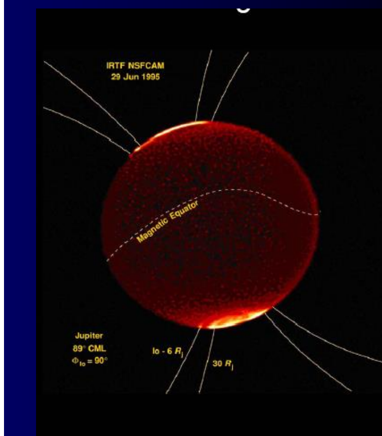
Different views
& different plasmas

# $H_3^+$ and its interaction of with $e^-$ is **FUNDAMENTAL**

If you understand hydrogen,
you understand all
that can be understood.
(*V. Weisskopf & G. Herzberg*).




J.E.P. Connerney and T. Satoh,
Phil. Trans. R. Soc. Lond. A358, 2471 (2000)

# Ion storage rings

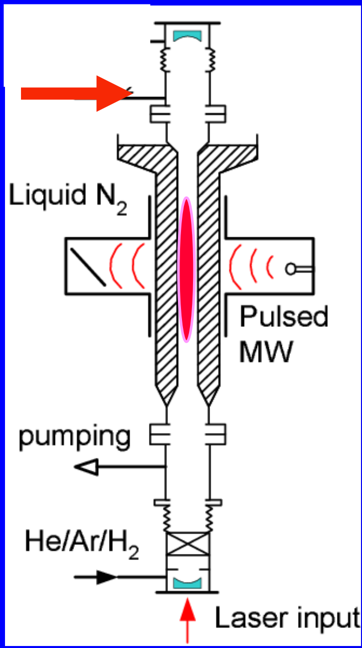
AISA

FALP

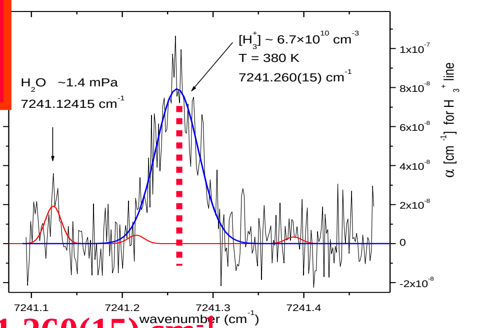
Quo vadis??

# Absorption studies

## $He/Ar/H_2/D_2$

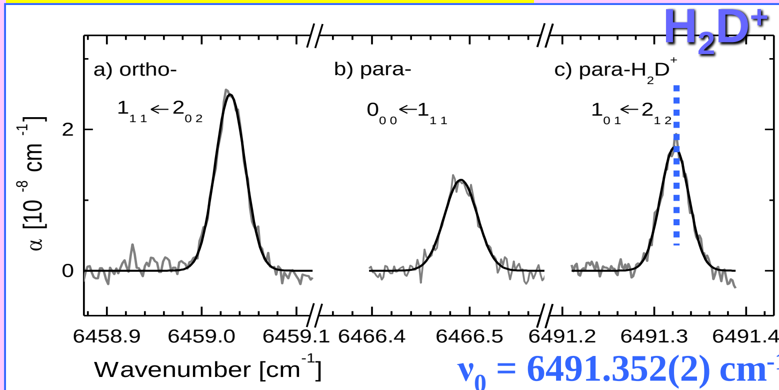



## $H_3^+$



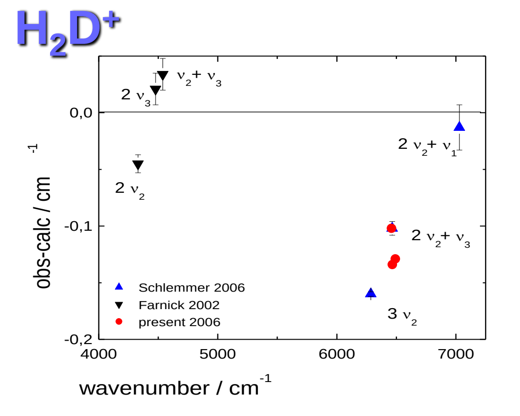

7241.260(15) cm$^{-1}$

## $H_2D^+$ $(2\nu_2 + \nu_3 \leftarrow 0)$

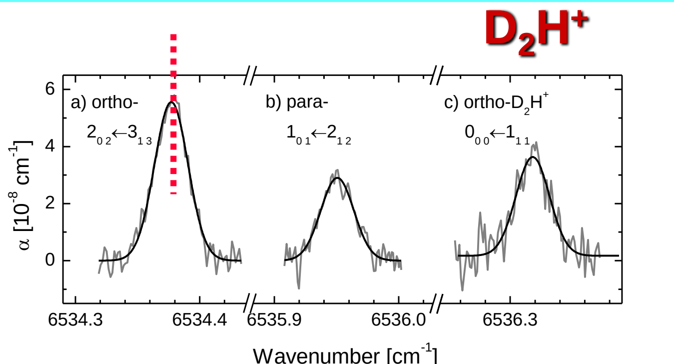



$\nu_0$ = 6491.352(2) cm$^{-1}$

Combination band



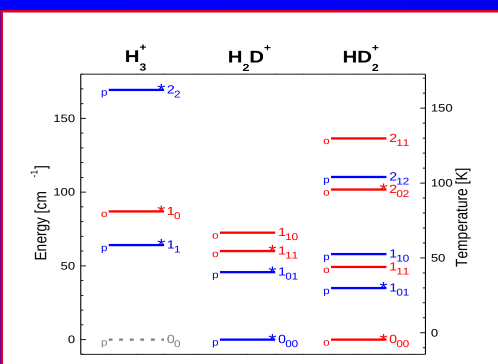

## $D_2H^+$ $(\nu_1 + 2\nu_3 \leftarrow 0)$




$\nu_0$ = 6534.377(1) cm$^{-1}$

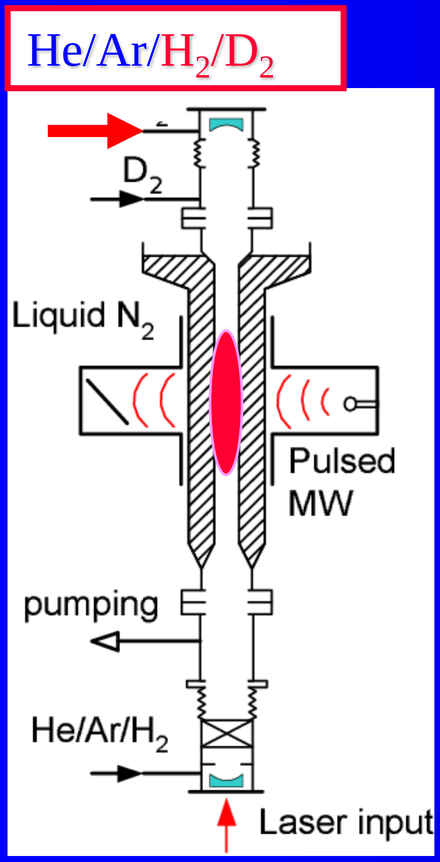
Combination band

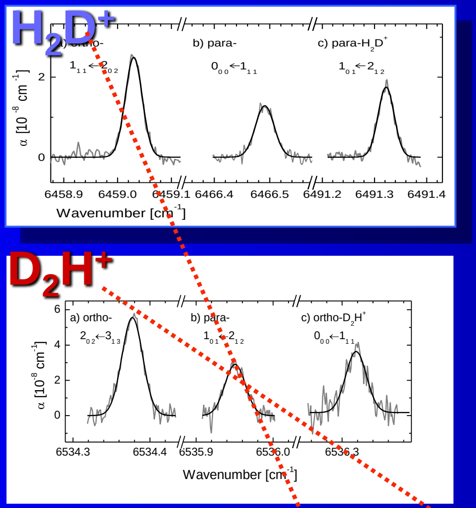
| E'[K] | Wavenumber [cm$^{-1}$] $\nu_{Exp}$ | $\nu_{Theor}$ | $\nu_{Theor} - \nu_{Exp}$ |
|---|---|---|---|
| 146.3 | 6534.377(1) | 6534.374 | 0.003 |
| 50.2 | 6535.950(1) | 6535.943 | 0.007 |
| 0 | 6536.319(2) | 6536.301 | 0.018 |

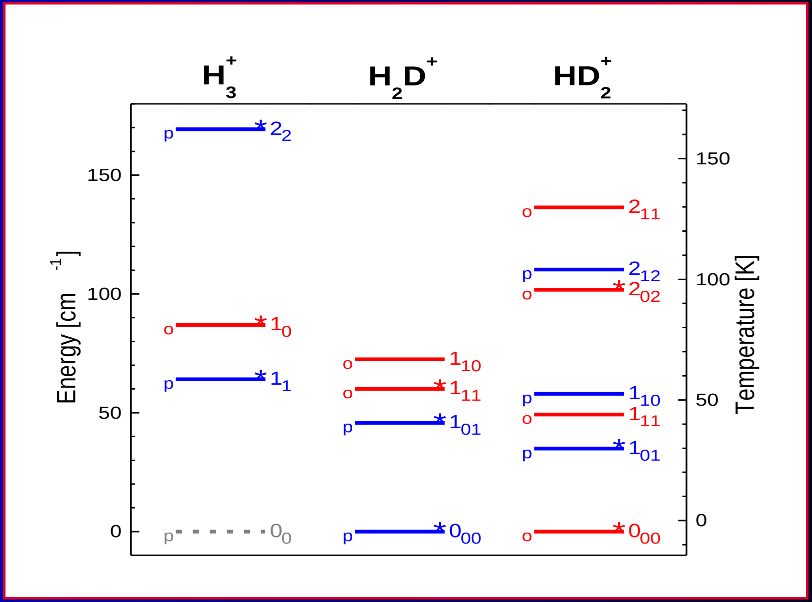


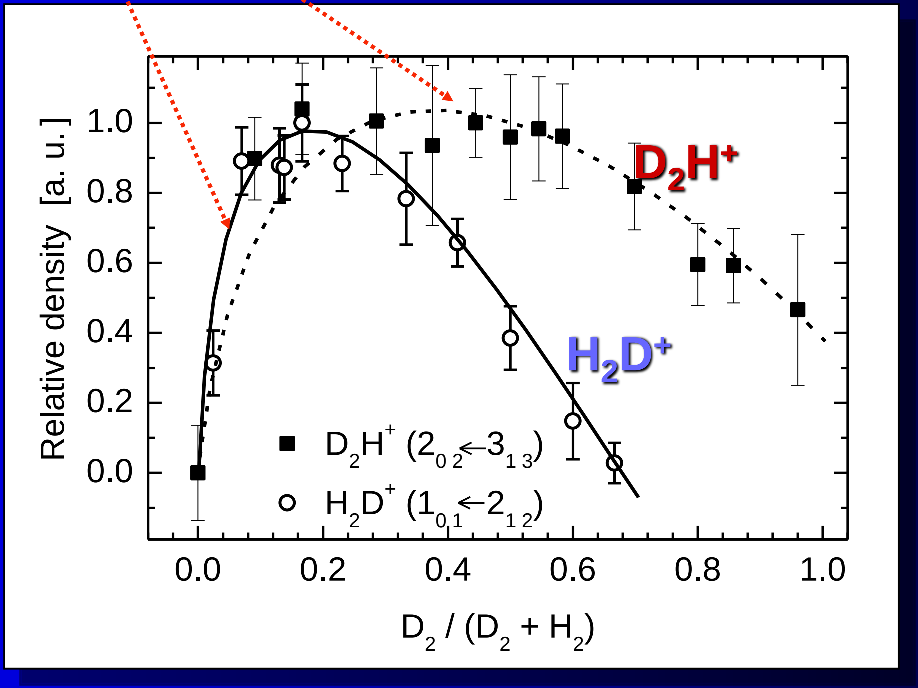

## $D_3^+$ ???

# Ionic composition of $H_2/D_2$ plasma



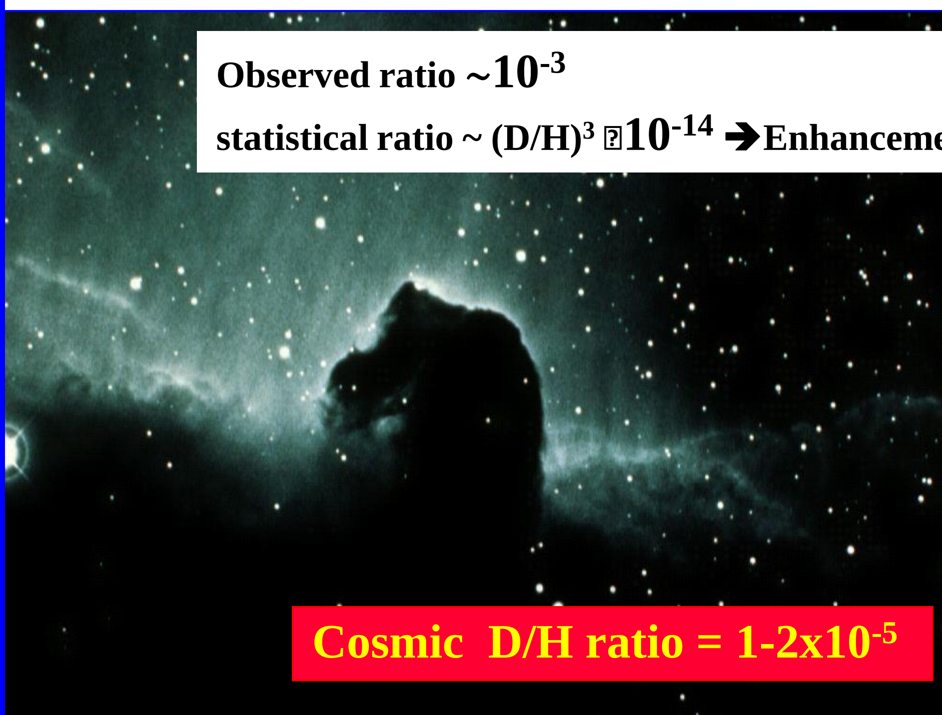



# Observation of high population of deuterated molecules

The first detection of deuterated molecules were made in the early 1970s……. Observed enhancement of D in molecules

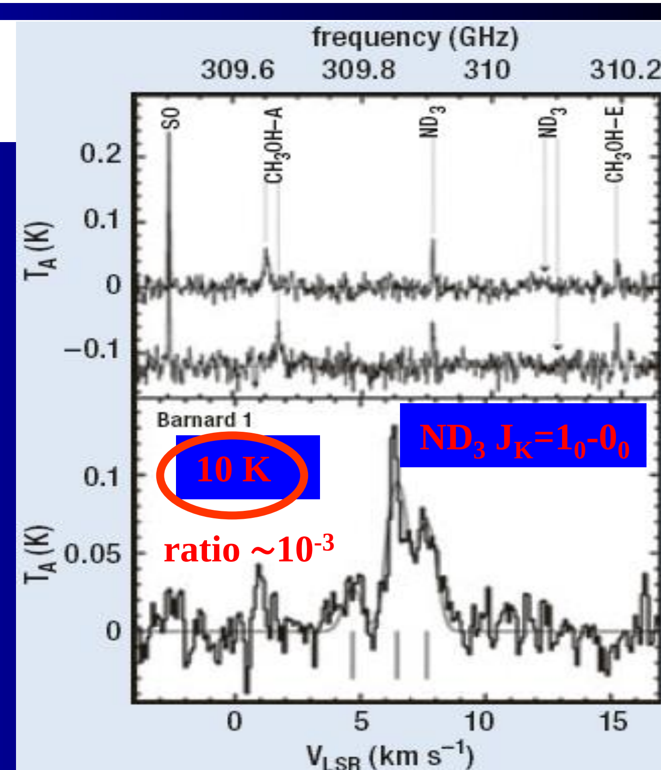
| | | | |
|---|---|---|---|
| $H_2D^+$ | Stark | (1999) | $1_{10}$–$1_{11}$ transition of ortho- emission from young stellar object NGC 1333 IRAS4A. |
| $H_2D^+$ | Caselli | (2003) | detected towards L1544. |
| $HD_2^+$ | Vastel | (2004) | the first detection |
| $CH_2DOH$… | Parise | (2003, 2004) | have detected 4 isotopomers of deuterated methanol |
| $NHD_2/NH_3$ | Roueff | (2000) | |
| | Loinard | (2001) | is 0.005 in the cold cloud L134N and 0.03 in the low-mass protostar 16293 E |
| $D_2CO/H_2CO$ | Loinard | (2002) | |
| | Bacmann | (2003) | is between 0.01 and 0.4 in a low-mass protostars and prestellar cores |
| $NH_2D/NH_3$ | J. Hatchell | (2003) | high ratios~4–33% in protostellar cores |
| $ND_3/NH_3$ | Lis | (2002) | ratio ~$10^{-3}$ cold dense Barnard 1cloud |
| | Tak | (2002) | Class 0 protostar NGC 1333 IRAS4A |



**Observed ratio ~$10^{-3}$**

**statistical ratio ~ $(D/H)^3$ ≈$10^{-14}$ ➔Enhancement of $10^{11}$**

**Cosmic D/H ratio = 1-2x$10^{-5}$**




2: Spectrum of $ND_3$ towards the dark cloud B1.
(Lis *et al.* 2002 *ApJ* 571 L55)

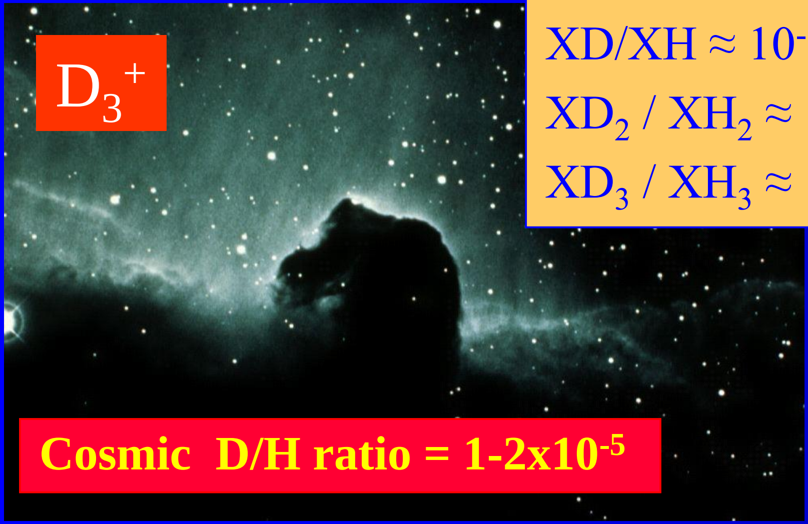
# High population of deuterated molecules

Cosmic D/H $\approx 10^{-5}$

XD/XH $\approx 10^{-1}$-$10^{-3}$

$XD_2$ / $XH_2 \approx 10^{-2}$

$XD_3$ / $XH_3 \approx 10^{-3}$




| Species | Observed ratio |
|---|---|
| $NH_2D/NH_3$ | 0.01 |
| $HDCO/H_2CO$ | 0.005-0.11 |
| DCN/HCN | 0.023 |
| DNC/HNC | 0.015 |
| $C_2D/C_2H$ | 0.01 |
| $DCO^+/HCO^+$ | 0.02 |
| $N_2D^+/N_2H^+$ | 0.08 |
| $DC_3N/HC_3N$ | 0.03-0.1 |
| $HDCS/H_2CS$ | 0.02 |

$H_3^+$ $D_3^+$

| | | |
|---|---|---|
| HD | $H_2D^+$ | $D_2H^+$ |
| $N_2D^+$ | $DCO^+$ | DCN |
| DNC | HDCS | $D_2CS$ |
| HDO | $DC_3N$ | $DC_5N$ |
| $C_3HD$ | HDCO | $D_2CO$ |
| $CH_3OD$ | $CH_2DOH$ | $CHD_2OH$ |
| $CD_3OH$ | $CH_2DCN$ | $NH_2D$ |
| $NHD_2$ | $ND_3$ | $CHD_2CCH$ |
| $CH_3CCD$ | $C_2D$ | $C_4D$ |
| HDS | $D_2S$ | |

**Deuterated molecules that have been detected in interstellar clouds as of February 2005.**

**Gas phase reactions,**

**ion-molecule reactions,**

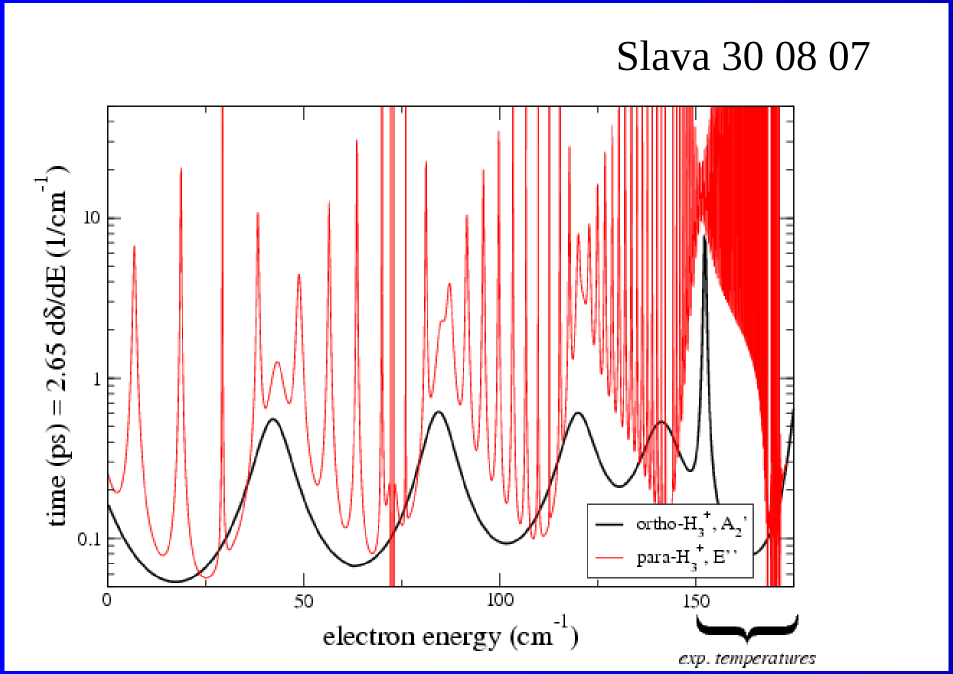
**recombination**

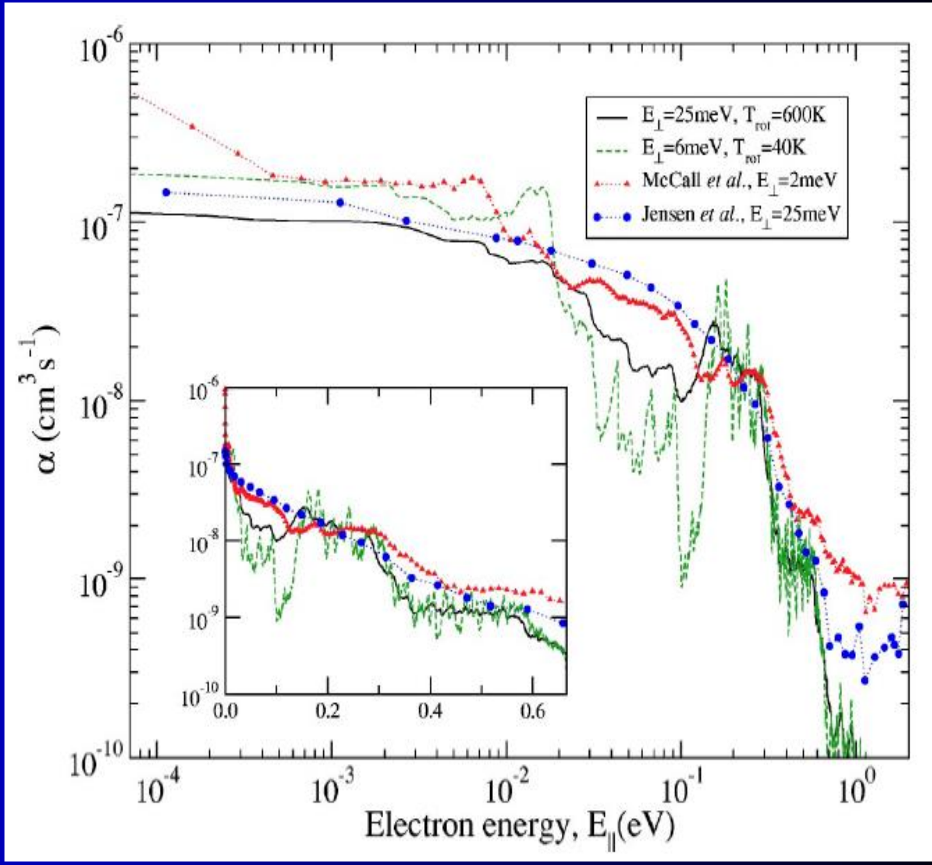
**Grain surface reactions**

**Physics of condensation and evaporation from grain surface**

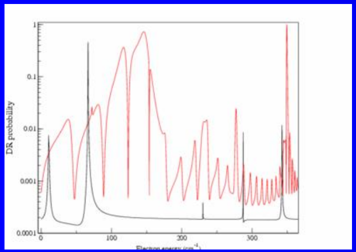
# Calculated life time from Slava

$$H_3^+ + e \rightarrow H_3^*$$




$$H_3^+ + e \Leftrightarrow H_3^* \rightarrow$$



Dear Juraj and Chris, I'm sending you the figure with the DR probabilities for two different symmetries (red and black curves). The red curve corresponds to the rotational autoionization region. Fro this figure you can have an idea about the widths of the resonances. With best wishes, Slava

# Recombination rate coefficients

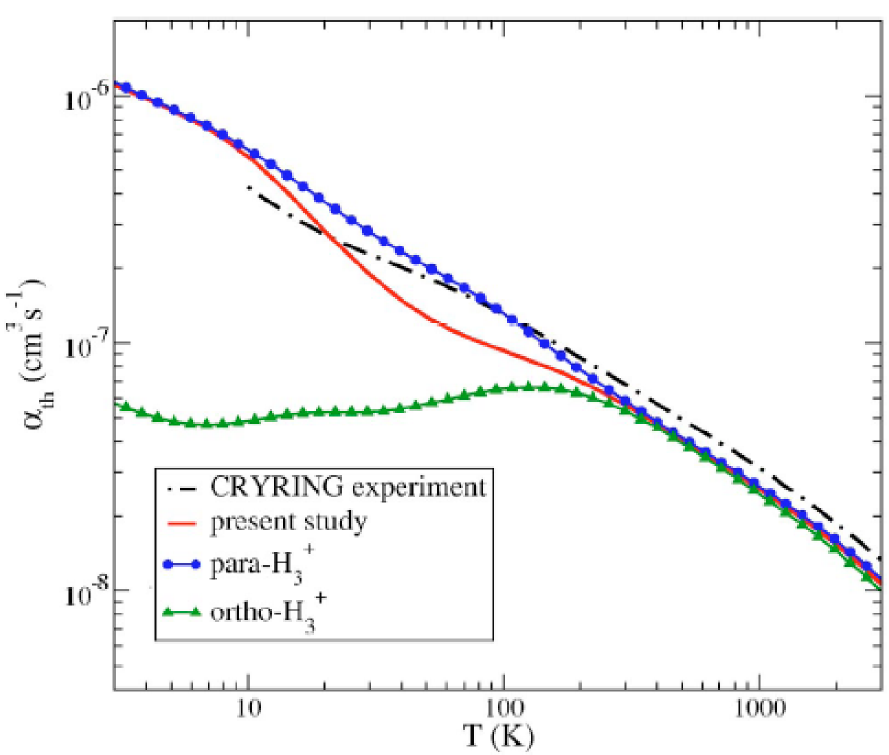



FIG. 5. (Color online) The present theoretical thermal rate coefficient for dissociative recombination of $H_3^+$ is compared with the experimental rate coefficient deduced from the storage ring experiment of McCall and co-workers (Refs. 9 and 10).

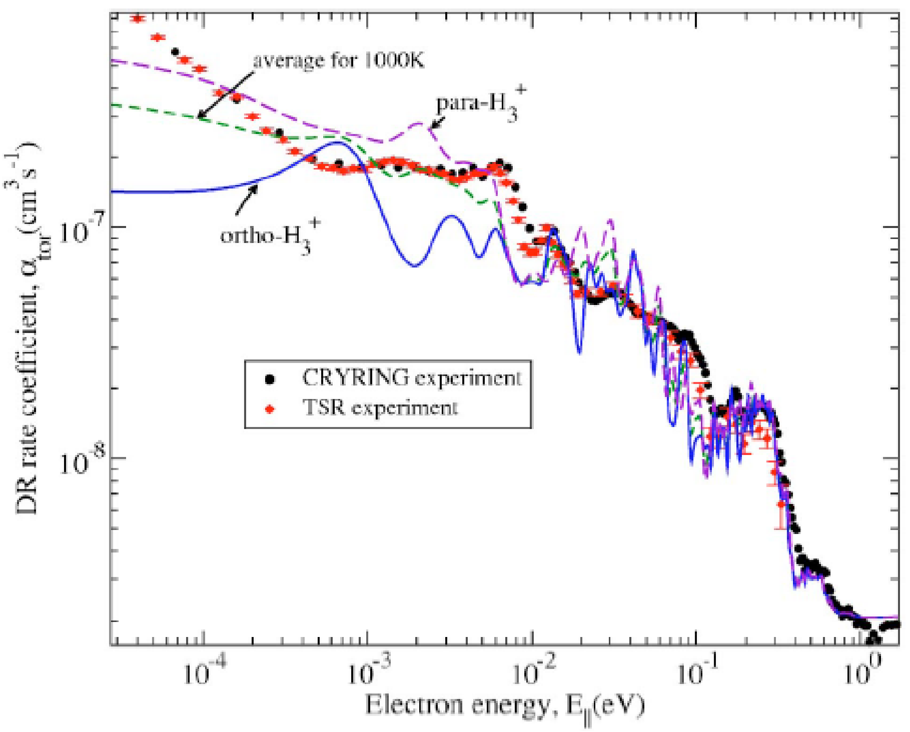
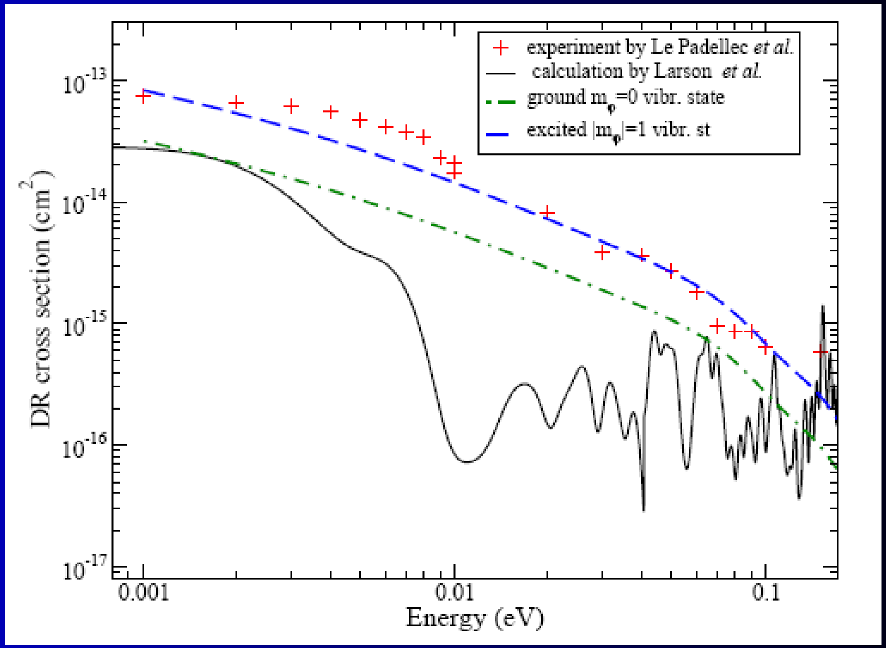
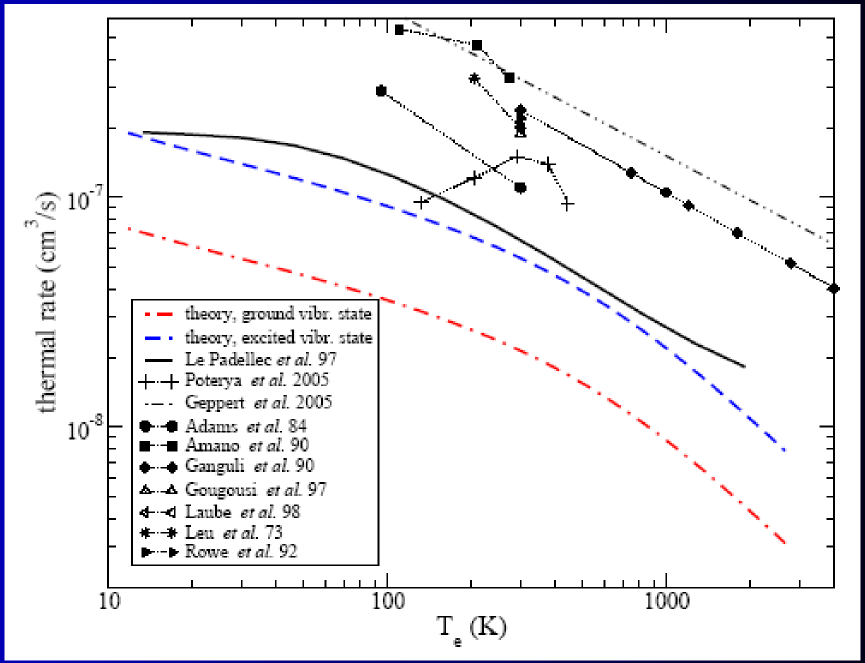



FIG. 3. (Color online) This figure compares the theoretical DR rate coefficient to the high-resolution storage ring experiment of Kreckel *et al.*[12] carried out at TSR. The experimental resolution parameters are $\Delta E_{\|}$ and $\Delta E_{\perp}$ are 25 $\mu$eV and 0.5 meV, respectively. The theoretical curve shown has been calculated with these parameters and rotational temperature $T_{rv}$ =1000 K. The figure also shows the theoretical DR rate coefficients calculated separately for ortho- and paraconfigurations of $H_3^+$ with the same parameters $\Delta E_{\|}$, $\Delta E_{\perp}$, and $T_{rv}$.

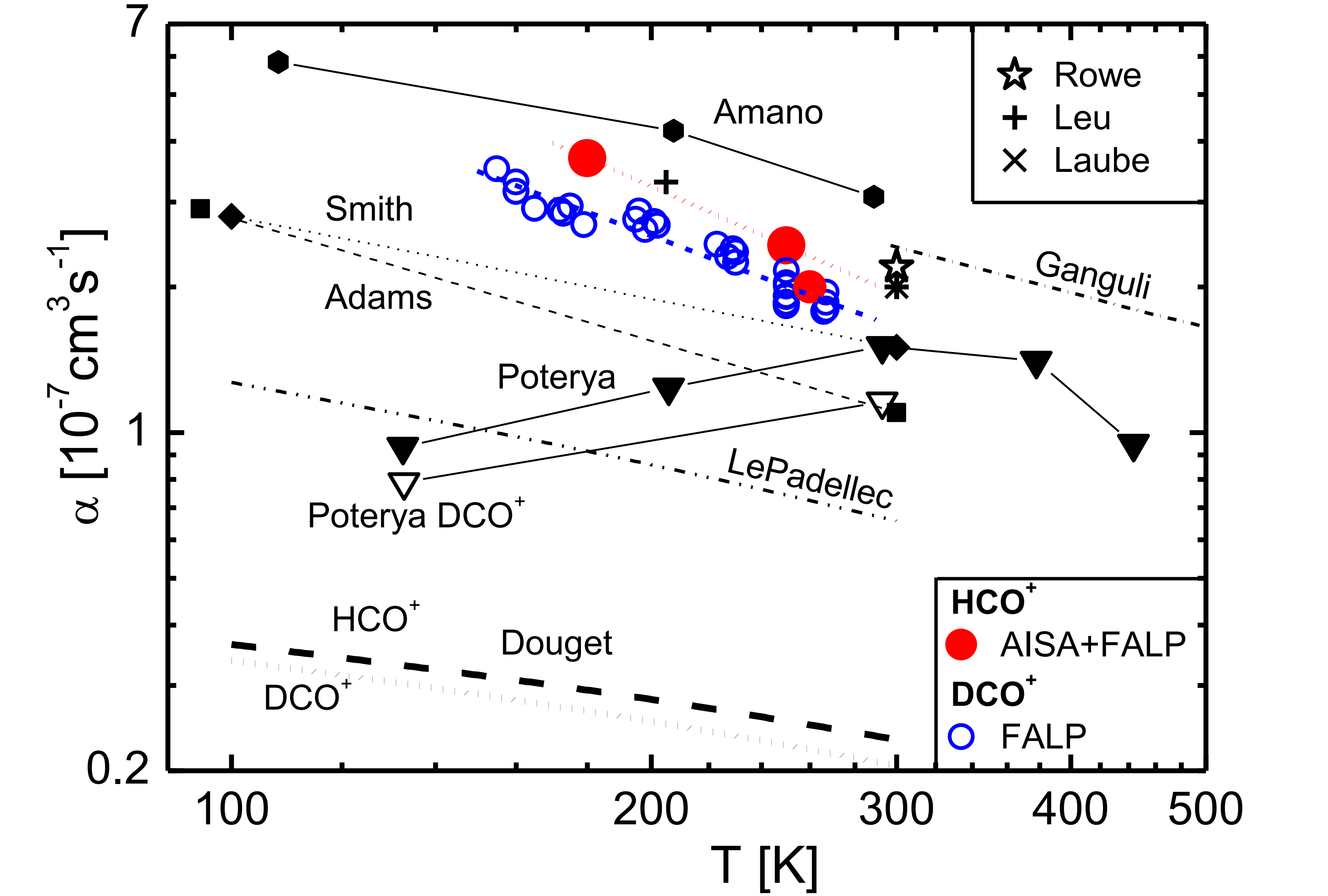
# Tunneling dissociative recombination

## $HCO^+$



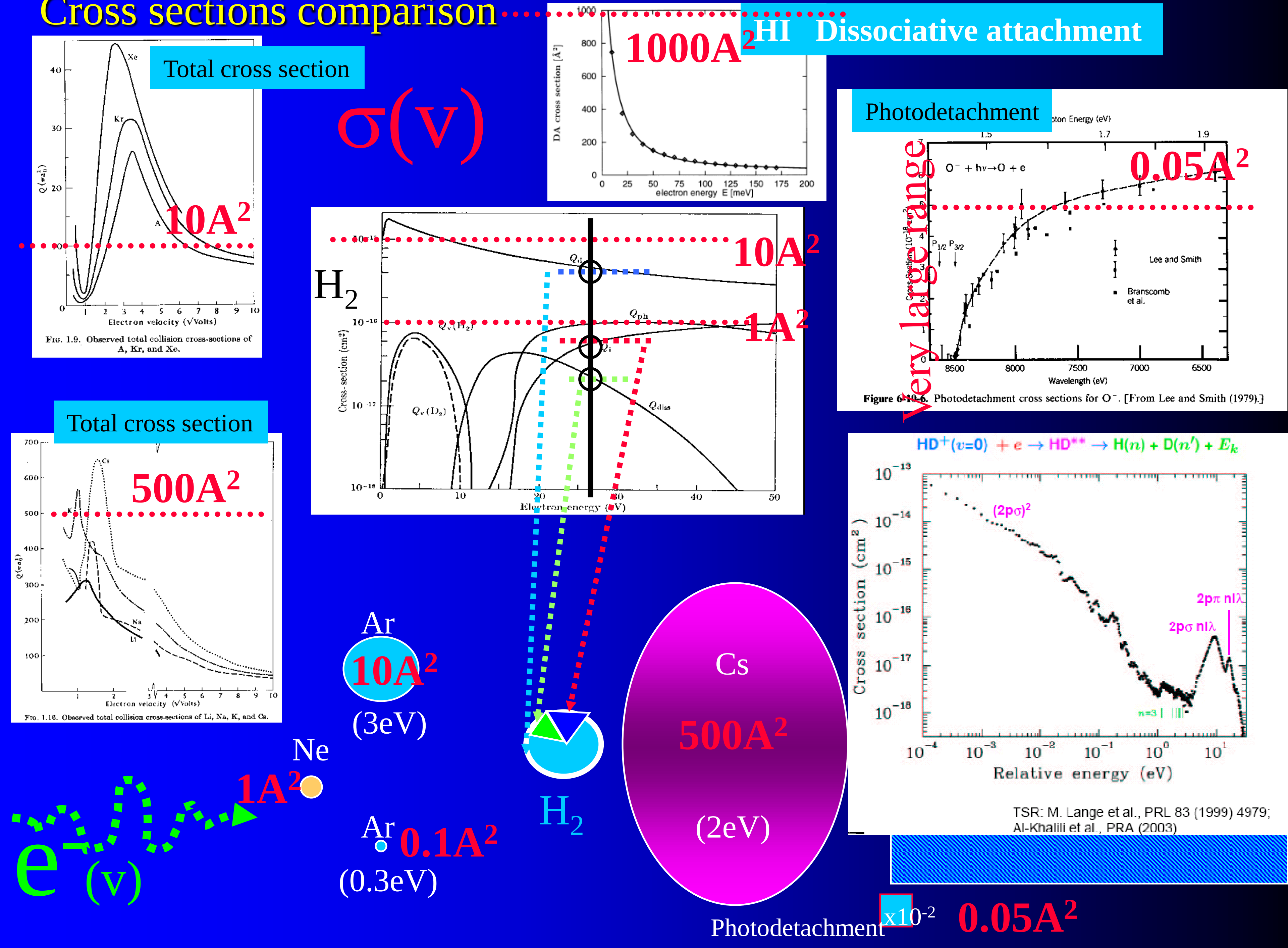
# Recombination of $HCO^+$ - state of the art



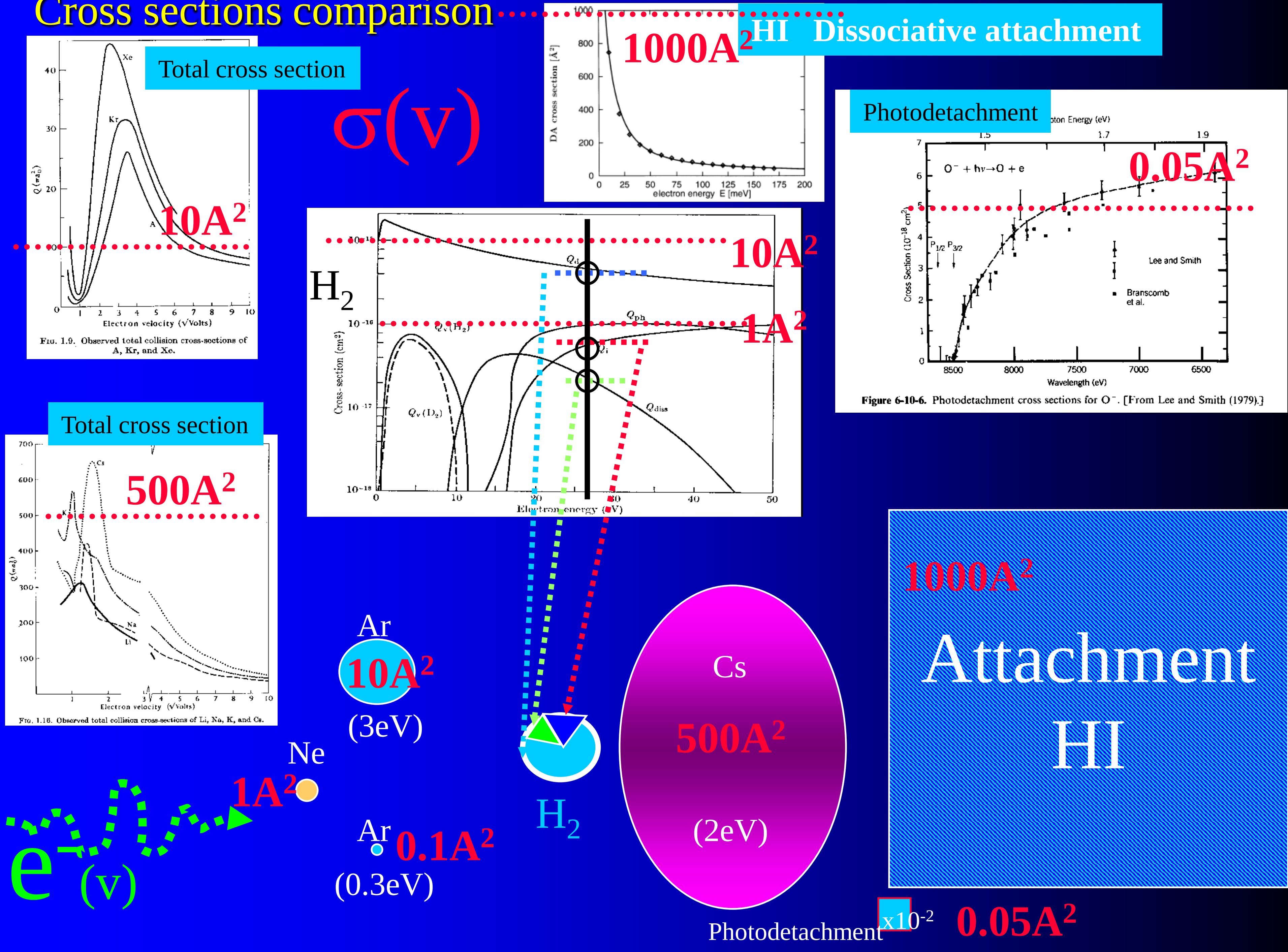

I. Korolov, at al.:*Int. J. Mass Spectom.* 280, 144 (2009)

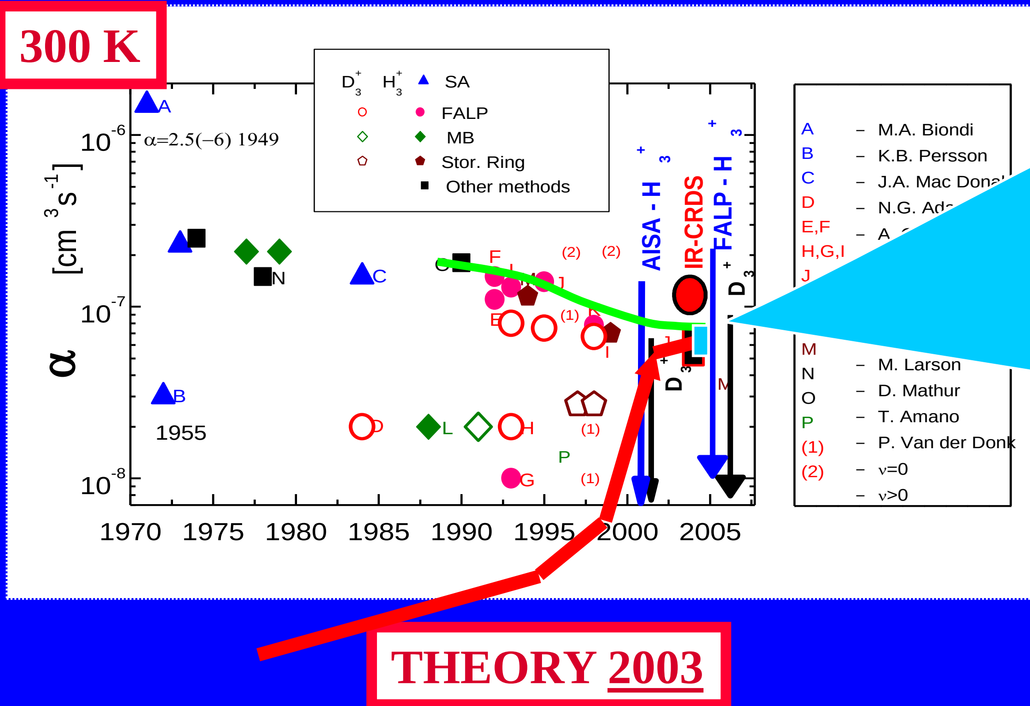
Do we really understand what is going on ????!!!!

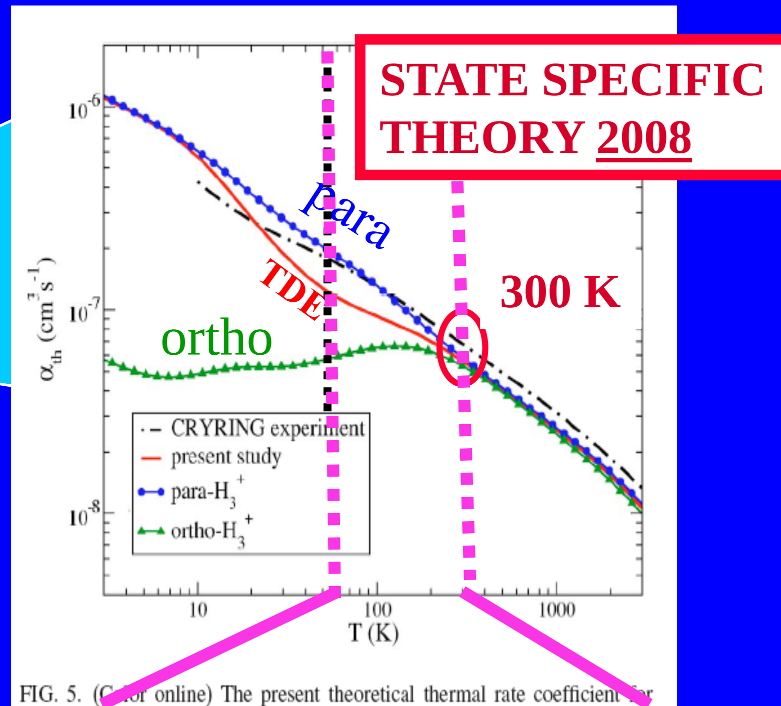
# Cross sections comparison



# Cross sections comparison






**b) DIFFUSE CLOUDS: DESTRUCTION:** $H_3^+ + e^-$

$d[H_3^+]/dt \sim -\alpha_{DR}[H_3^+][e^-]$

$[e^-] \sim [C]$

$\alpha_{DR} = 2\times10^{-7}\,cm^3s^{-1} \times (T/300)^{-0.65}$ ?

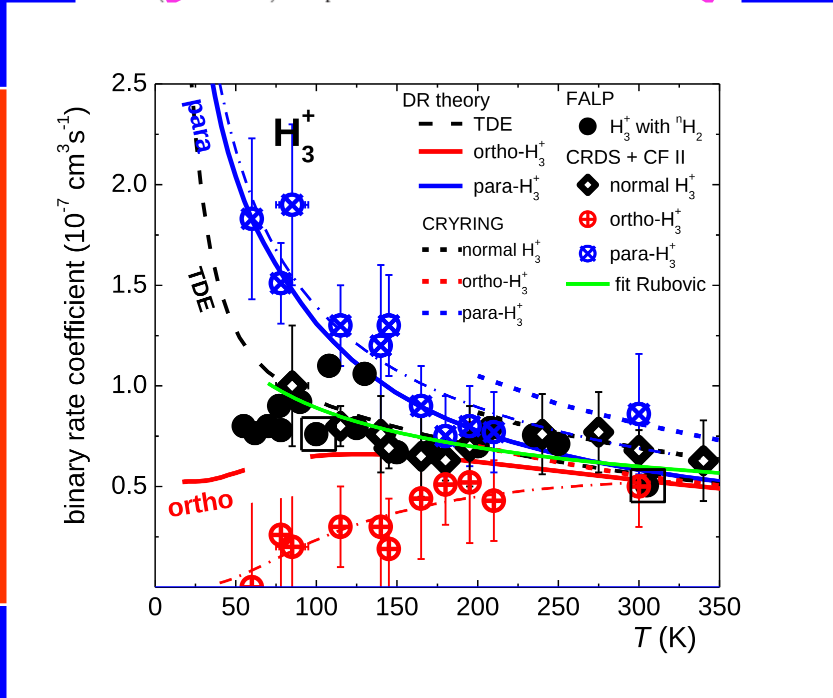
$[H_3^+] = \gamma/\alpha_{DR} \cdot [H_2]/[C] = \sim 1\times10^{-7}\,cm^{-3}$

~ NO with observation

?

$^p\alpha_{bin} = {^p\alpha_{bin}}(T)$

$^o\alpha_{bin} = {^o\alpha_{bin}}(T)$

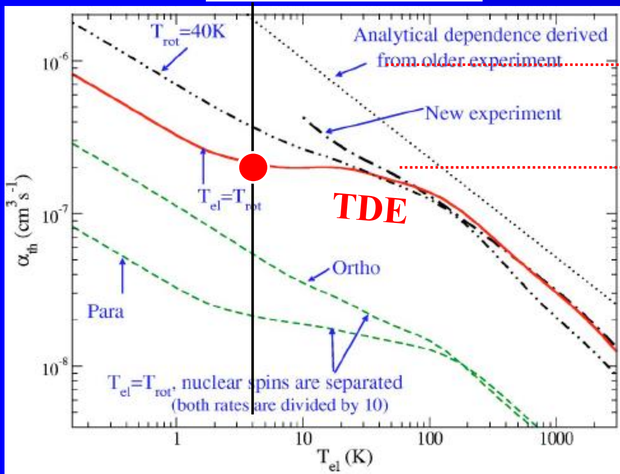



State of the art – 1st December 2014

# New "state selective" study with "cold ion source" observed faster recombination of para $H_3^+$ in comparison with ortho $H_3^+$ ……

B. J. McCall, et al. *Physical Review A* (2004)    H. Kreckel, et al. Phys. Rev. Lett. 2005,

**Before 2007**




**2008, new improved calculations**

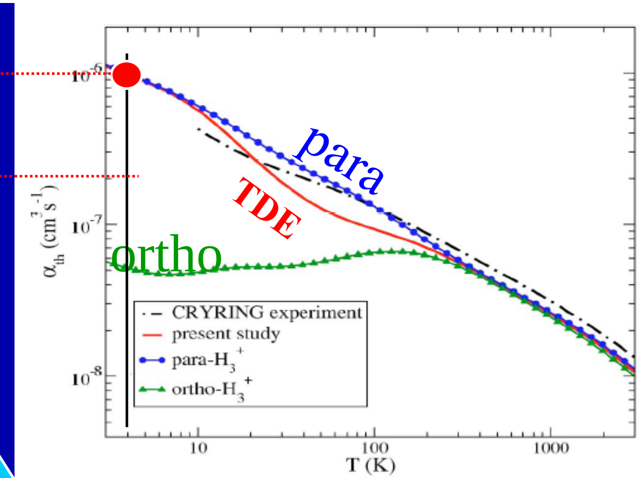


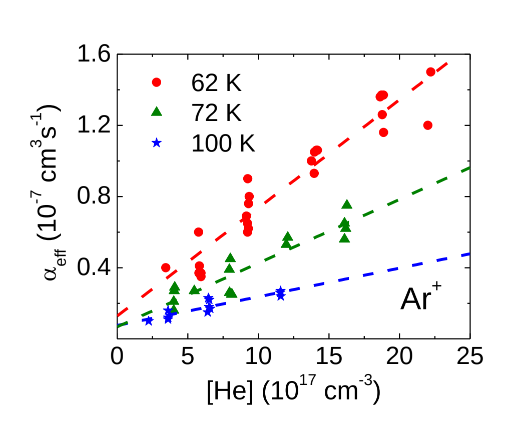

FIG. 5. (Color online) The present theoretical thermal rate coefficient for dissociative recombination of $H_3^+$ is compared with the experimental rate coefficient deduced from the storage ring experiment of McCall and co-workers (Refs. 9 and 10).

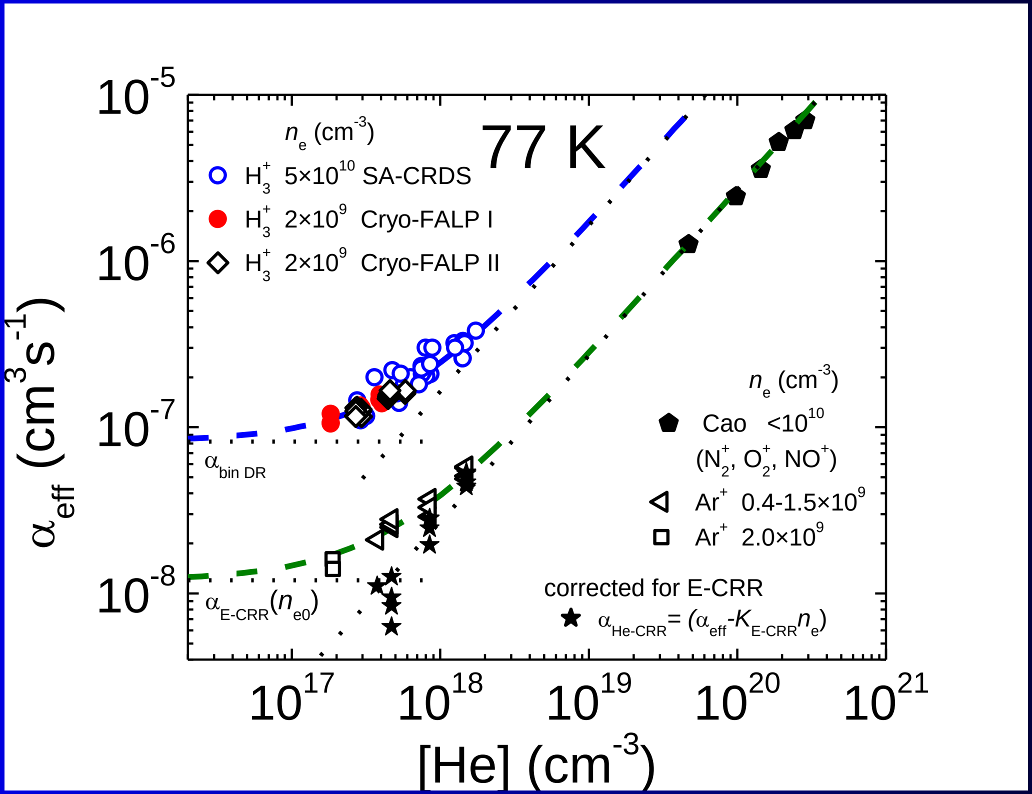
<u>**In the middle of 2008**</u> M. Larsson et al wrote the Frontier article to Chem. Phys. Let., [Larsson 2008].

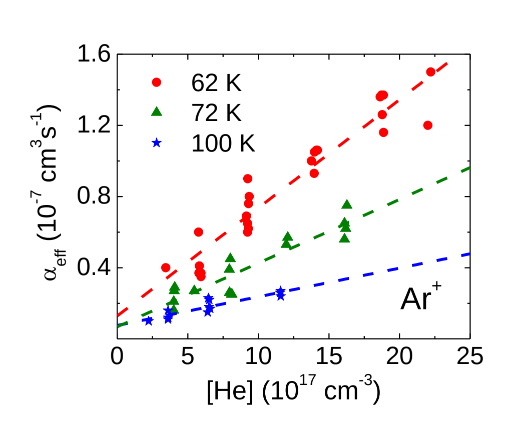
This was written in the abstract:
"…. *<u>Two independent ion storage ring experiments with rovibrationally cold H3+ ions are in excellent agreement</u>, and quantum mechanical calculations agree with the storage ring results quantitatively for the thermal rate constant, <u>if not in all details</u> concerning the cross section. <u>**The recombination mechanism is understood.**</u> A direct consequence of this progress is that the cosmic-ray ionization rate in diffuse clouds must be shifted upwards to a value larger than $10^{-16} s^{-1}$. …* "

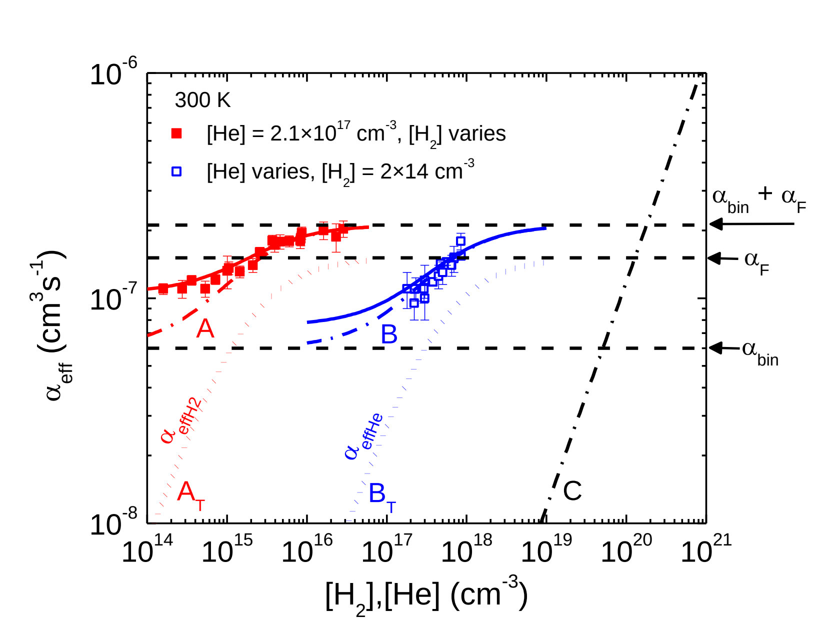
**In the abstract of [Petrignani 2010] it is written:**
*"… A systematic experimental assessment of <u>heating effects</u> is performed which, together with a survey of other <u>recent storage-ring data, suggests that the present rotationally cool rate-coefficient measurement was performed at 380 (+50 -130) K and that this is the lowest rotational temperature so far realized in storage-ring rate-coefficient measurements on H3+….</u>*

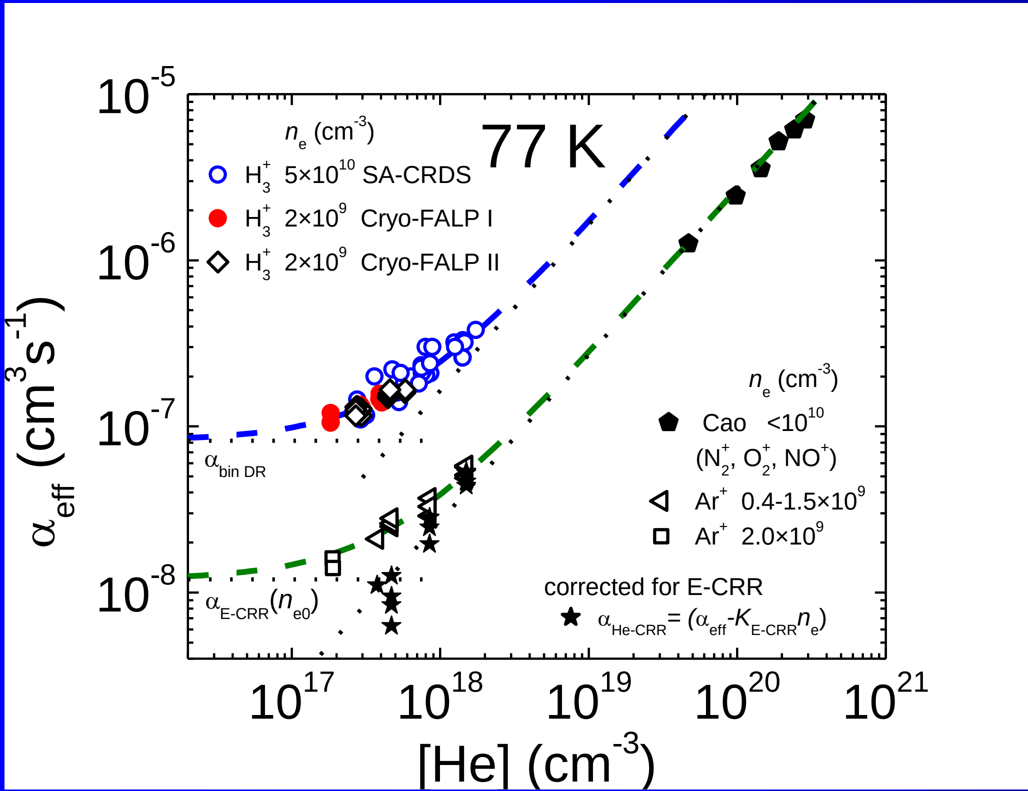
…. Unfortunately the experiments on storage rings were stopped …. ☹ ... ☹…


1.6
1.2
0.8
0.4
62 K
72 K
100 K
αeff (10-7 cm3s-1)
Ar+
0
5
10
15
20
25
[He] (1017 cm-3)


10-5
10-6
10-7
10-8
αeff (cm3s-1)
ne (cm-3)
77 K
H3+ 5×1010 SA-CRDS
H3+ 2×109 Cryo-FALP I
H3+ 2×109 Cryo-FALP II
αbin DR
αE-CRR(ne0)
ne (cm-3)
Cao <1010
(N2+, O2+, NO+)
Ar+ 0.4-1.5×109
Ar+ 2.0×109
corrected for E-CRR
αHe-CRR= (αeff-KE-CRRne)
1017
1018
1019
1020
1021
[He] (cm-3)


62 K
72 K
100 K
Ar+
αeff (10-7 cm3s-1)
[He] (1017 cm-3)


300 K
[He] = 2.1×1017 cm-3, [H2] varies
[He] varies, [H2] = 2×14 cm-3
αbin + αF
αF
αbin
A
B
C
AT
BT
αeffH2
αeffHe
αeff (cm3s-1)
[H2],[He] (cm-3)


77 K
ne (cm-3)
H3+ 5×1010 SA-CRDS
H3+ 2×109 Cryo-FALP I
H3+ 2×109 Cryo-FALP II
ne (cm-3)
Cao <1010
(N2+, O2+, NO+)
Ar+ 0.4-1.5×109
Ar+ 2.0×109
corrected for E-CRR
αHe-CRR= (αeff-KE-CRRne)
αbin DR
αE-CRR(ne0)
αeff (cm3s-1)
[He] (cm-3)