Kinetic Processes in Recombining H_3^+ plasmas

Rainer Johnsen

University of Pittsburgh

We have made tremendous progress, but the H_3^+ enigma is still with us

1995: T. Gougousi, M.F. Golde, and R. Johnsen, Int. J. Mass Spectr. 149, 131 (1995)

"Our [afterglow] measurements indicate that the de-ionization coefficient in the range (1.5 -2.5 x 10^{-7} cm^3/s may be appropriate for modeling H_3^+ plasmas of reasonably high densities and perhaps in some planetary atmospheres.
It is an entirely different question which recombination coefficient should be used in environments of very low density, e.g. in the interstellar medium. Here, the true binary recombination coefficient at low temperatures is needed. It is conceivable that the recombination cross sections measured in ion storage rings are close to the true values, but this is far from obvious, since the presence of electric fields in the interaction region may also lead to l-mixing effects"

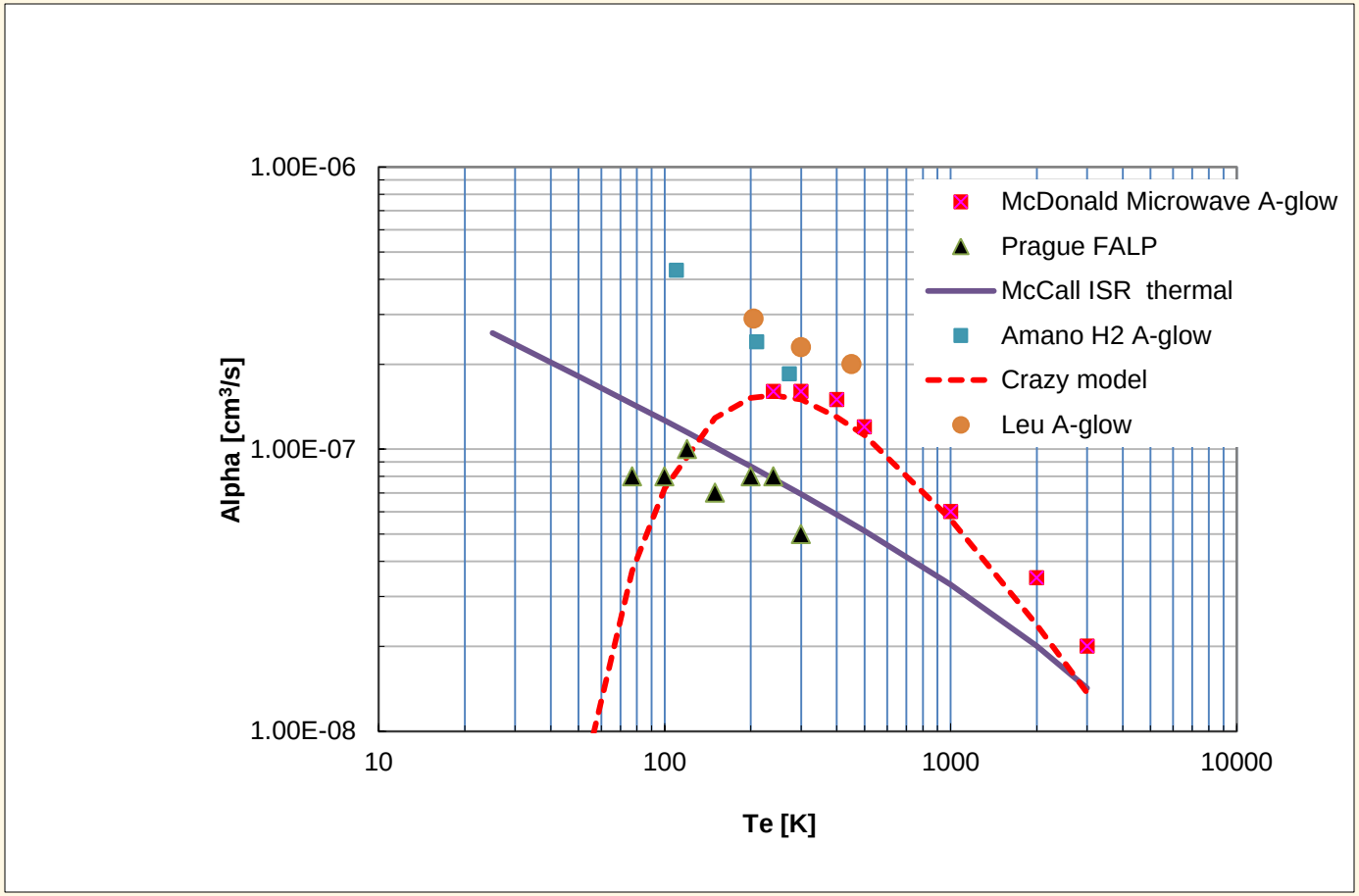
2011: A. Petrignani et al., Phys. Rev. A 83, 032711 (2011)

"A working hypothesis concerning the low-energy discrepancy between theory and experiment in Fig. 5a is that something problematic must be occurring in the treatment or the detection of the very highest Rydberg states in theory or experiment."

"…… in this case what should be explored is the possibility that either the Rydberg states are destroyed or the angular momentum quantum numbers are changed by external fields in the storage ring"

"Presently no rate coefficient measurement with a confirmed temperature below 300 K exists".
[not quite true!]

The observed recombination coefficients depend on gas composition and density. Why?



Notes:

McDonald data taken in 20 Torr Neon

Prague afterglow corrected for 3-body effect due to helium

Amano data taken in pure H2

My very old “Crazy model” to fit McDonald data

Both afterglows and storage rings have strengths and weaknesses

- Afterglows keep particles in thermal equilibrium
- Spectroscopy can be done easily in afterglows
- But third-body effects can affect recombination

- Storage rings have high energy resolution
- But is difficult to characterize rotational and para/ortho state abundances

How can the “afterglow plasma environment” change recombination?

Typical gas mixtures:

- Pure hydrogen
- One rare gas + hydrogen
- Helium+ argon+ hydrogen

Two types of afterglows:

Stationary: Hydrogen exposed to discharge and may stay vibrationally hot

Flowing: Hydrogen not exposed to discharge

The role of H_2 in afterglows:

$[H_2]$ must be high enough to produce H_3^+

much faster than it is lost by recombination.

Otherwise, H_3^+ is not the dominant ions

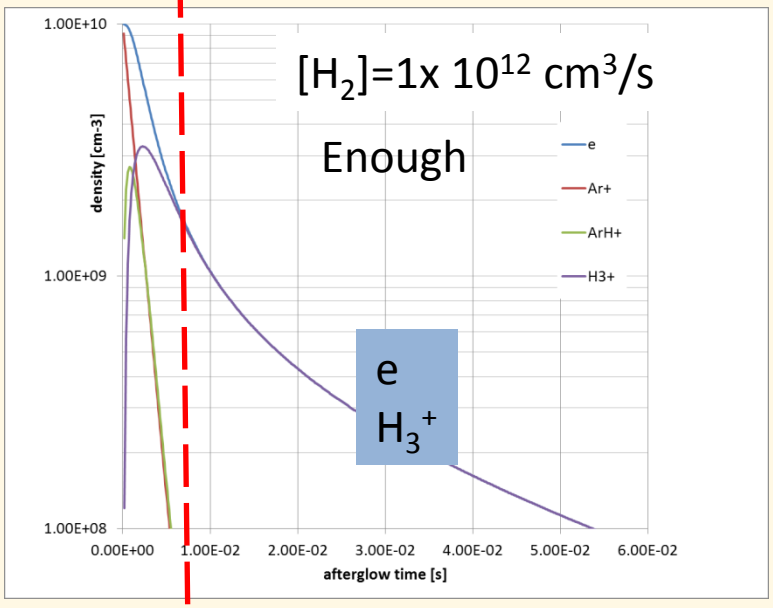
Production:

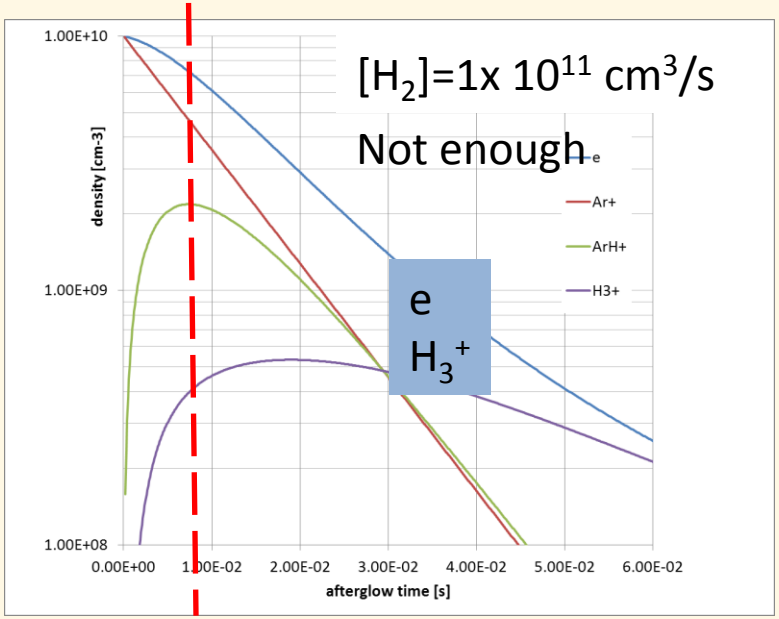
$$Ar^+ + H_2 \rightarrow ArH^+ + H$$

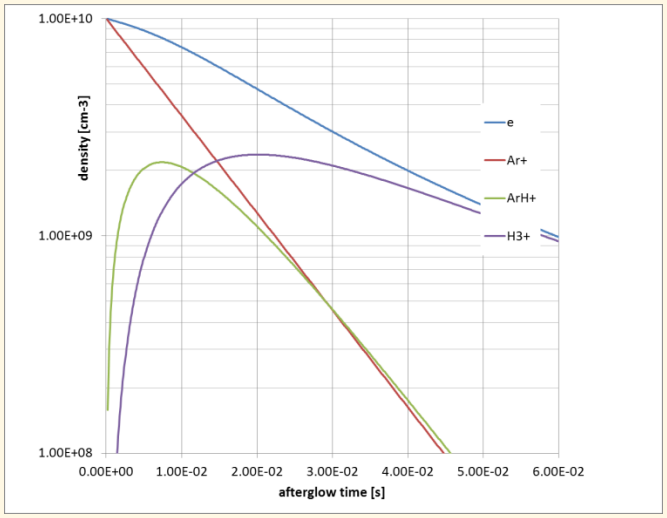
$$ArH^+ + H_2 \rightarrow Ar + H_3^+$$

Loss:

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

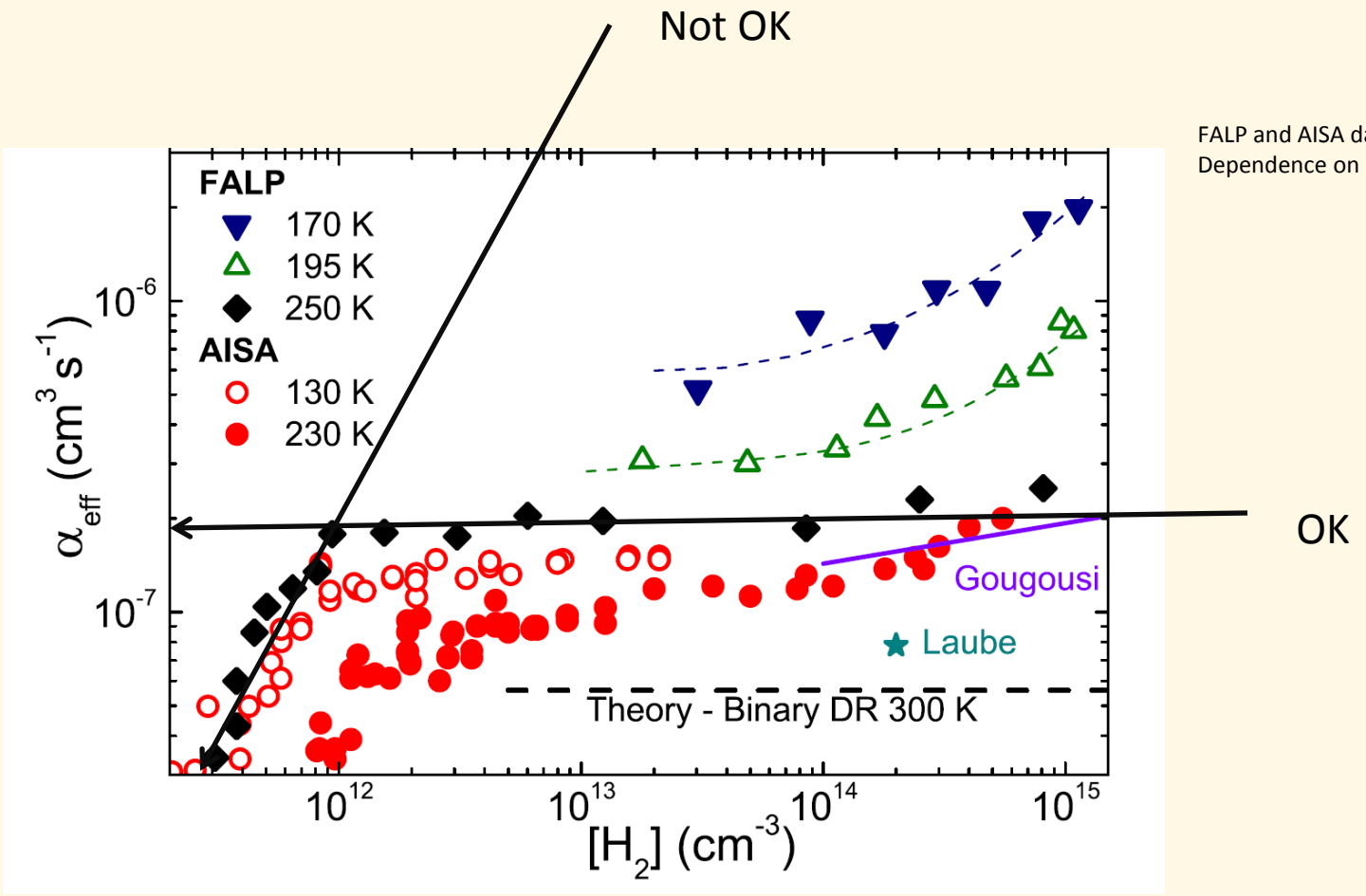






[H2]= 1e11 but alpha = 1e-8

If $[H_2]$ is too low, one gets recombination coefficients that are too small!



FALP and AISA data from Prague
Dependence on $[H_2]$

Question: To get the binary recombination coefficient, should we extrapolate to $[H_2]=0$?

Or should we take the value where alpha is nearly independent of $[H_2]$?

√

What else does H_2 do during the afterglow?

The reaction:

$$H_3^+ + H_2 \leftrightarrow (H_5^+)^*$$

Keeps rotational states and the para/ortho ratio constant during the afterglow, even if recombination depends on rotational states and para-ortho ratio.

The data obtained in Prague show that $[H_2] \sim 10^{14}$ cm^{-3} is enough.

But: At low temperatures one has to worry about H_5^+.
It recombines about 20 times faster that H_3^+.

$$H_3^+ + H_2 + M \leftrightarrow H_5^+ + M$$

$$H_3^+ + H_2 + M \leftrightarrow H_5^+ + M$$

Equilibrium constant *vs* T

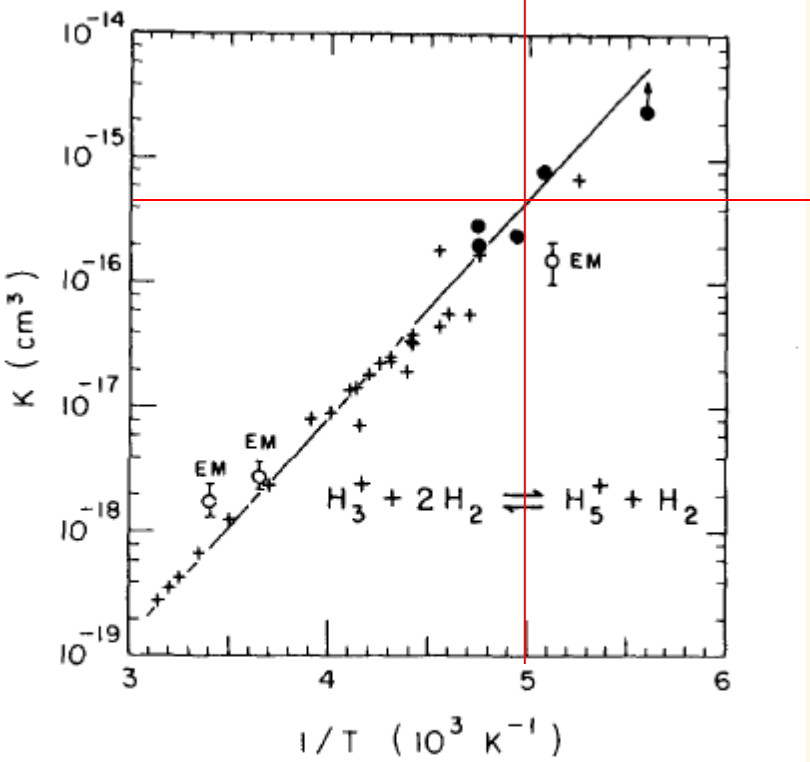


FIG. 1. Van't Hoff plot of log K vs T^{-1}. The experimental values are accurate to ±50%. Data obtained from H_3^+ decays, solid dots; data from $[H_5^+]/[H_3^+]$ ratios, + symbols. Points marked EM are from Ref. 5.

Example:
T=200 K, $[H_2] \sim 10^{14}$ cm^{-3}

$[H_5^+]/[H_3^+] \sim 4\%$

About 50% of recombination loss would be due to H_5^+ !

Worse at lower T and higher $[H_2]$

Johnsen, Huang, Biondi
JCP 65, 1539 (1976)

But: The chemical equilibrium is approached fairly slowly.
One needs to make a model the afterglow! The relevant rates are fairly well known.

$$H_3^+ + H_2 + H_2 \rightarrow H_5^+ + H_2$$

$$H_3^+ + H_2 \leftarrow H_5^+ + H_2$$

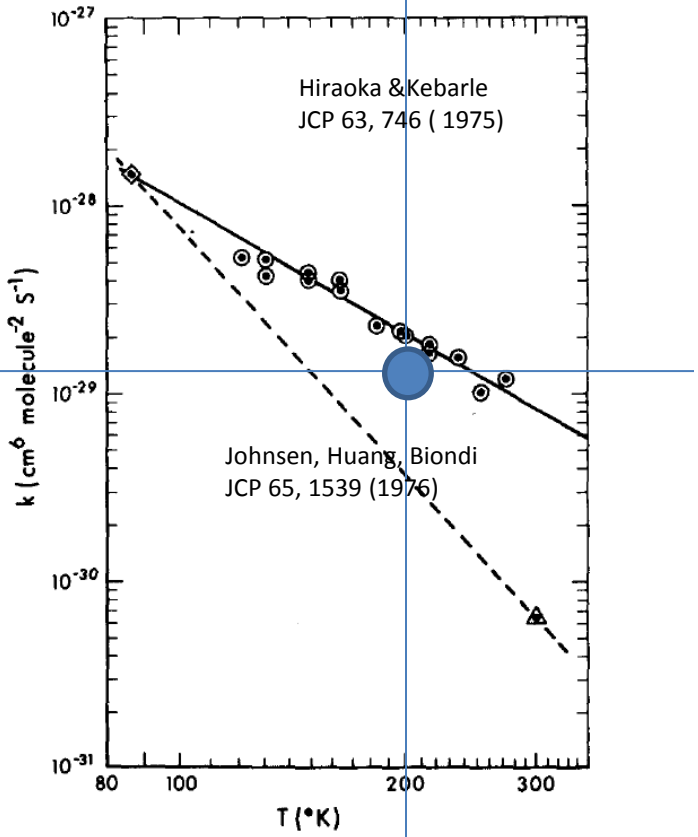


FIG. 2. Logk_1 versus log$T$ plot of rate constant for reaction $H_3^+ + 2H_2 = H_5^+ + H_2$. o present work; ◇ Pierce and Porter.[1] Δ Arifov.[2]

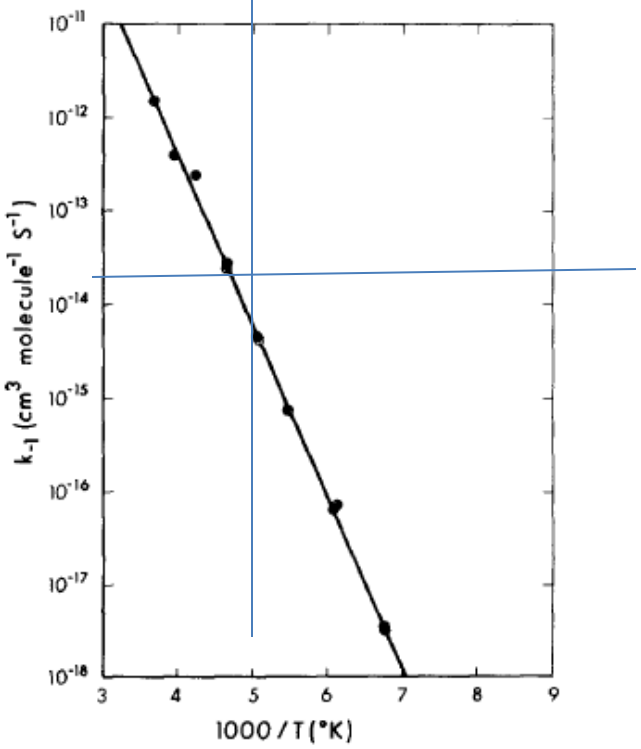


FIG. 3. Arrhenius plot of rate constant k_{-1} for thermal decomposition of H_5^+ at low pressures where thermal activation is second order. (-1) $H_5^+ + H_2 = H_3^+ + H_2$. Straight line leads to $k_{-1} = 8.7 \times 10^{-7} \exp(-8.4/RT)$ cm^3 where activation energy in kcal/mole and k_{-1} in cm^3 molecules^{-1} · sec^{-1}.

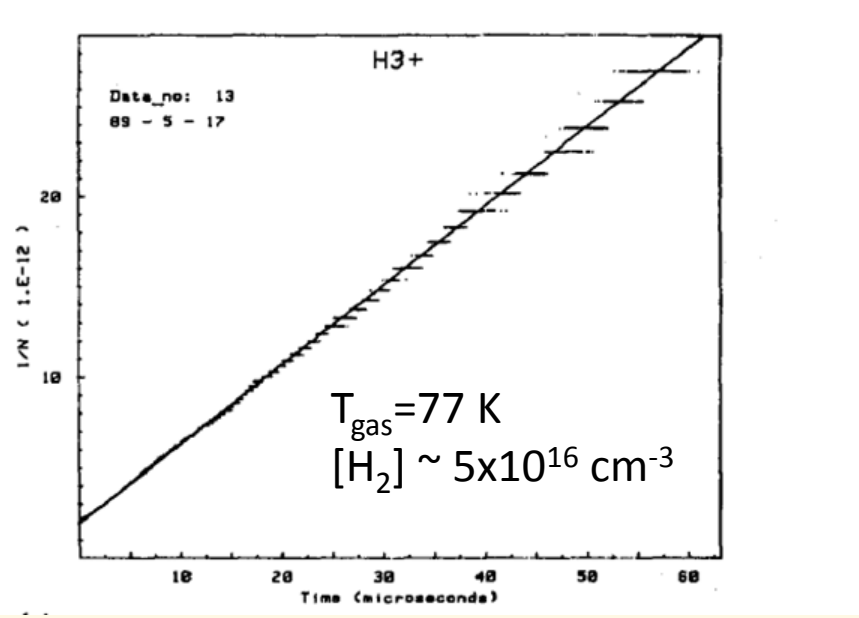
The dissociative recombination rate coefficients of H_3^+, HN_2^+, and HCO^+

T. Amano
Herzberg Institute of Astrophysics, National Research Council, Ottawa, Canada K1A 0R6

(Received 24 August 1989; accepted 23 February 1990)

Discharge afterglow in pure H_2 . Infrared absorption by H_3^+

The graphs of 1/ [H3+] vs time were compatible binary recombination



T_{gas}=77 K
$[H_2]$ ~ 5x10^{16} cm^{-3}

Rate coefficients ~ 4.3 x 10^{-7} at T_e=110 K

TABLE I. The dissociative recombination rate coefficients of H_3^+ in the ground vibrational state (in units of 10^{-7} cm^3 s^{-1}).

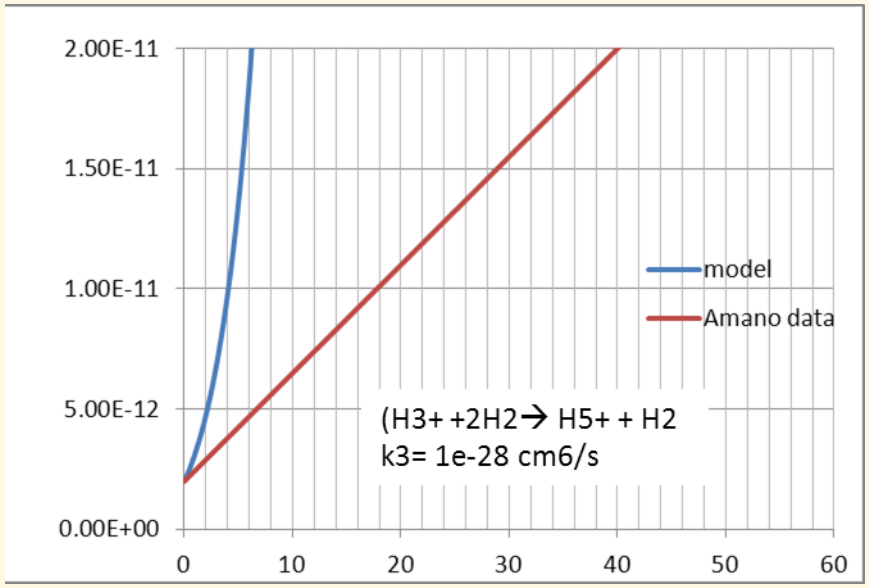
J, *K*	110 K	210 K	273 K
1, 0	4.1(2)[a]	2.5(1)	1.72(5)
1, 1	4.1(1)	2.7(2)	1.77(10)
2, 2	4.6(4)	2.4(2)	1.85(6)
3, 3	4.5(5)	2.6(2)	1.91(7)
4, 4	...	2.2(2)	1.9(4)

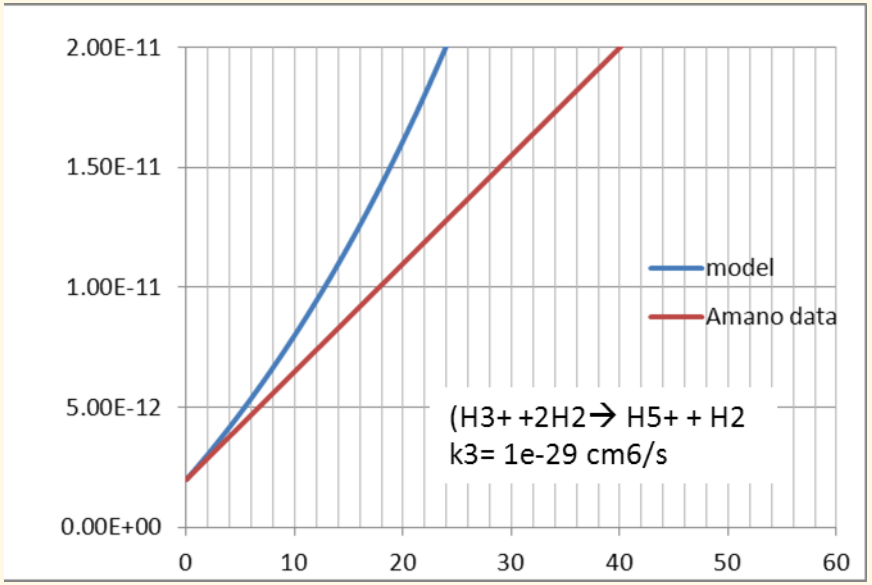
In my opinion, the observed recombination loss was not due to binary recombination of H_3^+.

In my opinion, the observed recombination loss was not due to binary recombination of H_3^+.

Problem #1: Why did the H_3^+ ions not convert to H_5^+

The decay should have looked like the blue lines





Using Kebarle's rate at 77 K

Using 0.1 * Kebarle's rate at 77 K

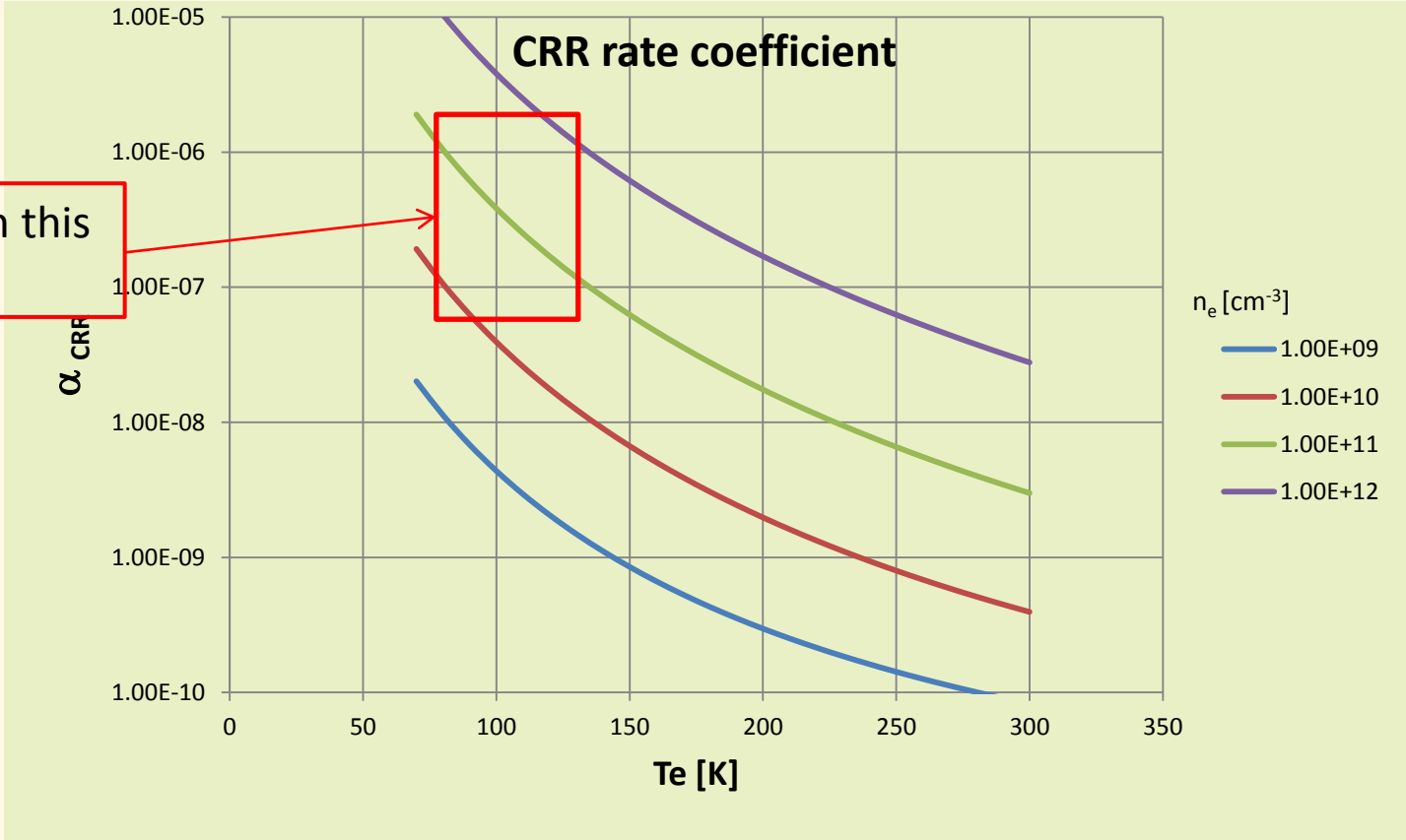
There must be something in the afterglow that reverses H5+ formation

Problem #2: Why did the H_3^+ ions not recombine by collisional radiative recombination?
The effective recombination rate should have dropped in the later afterglow.

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

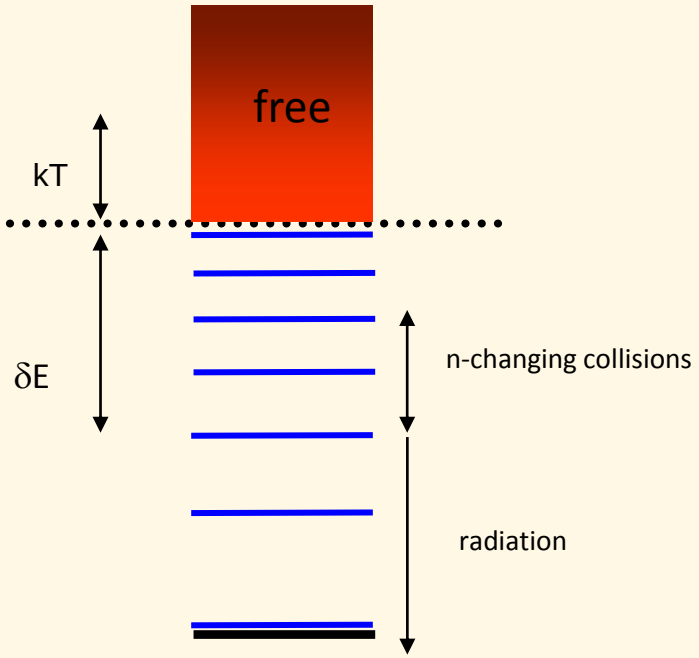
[cm^3/s] collisions radiation correction term

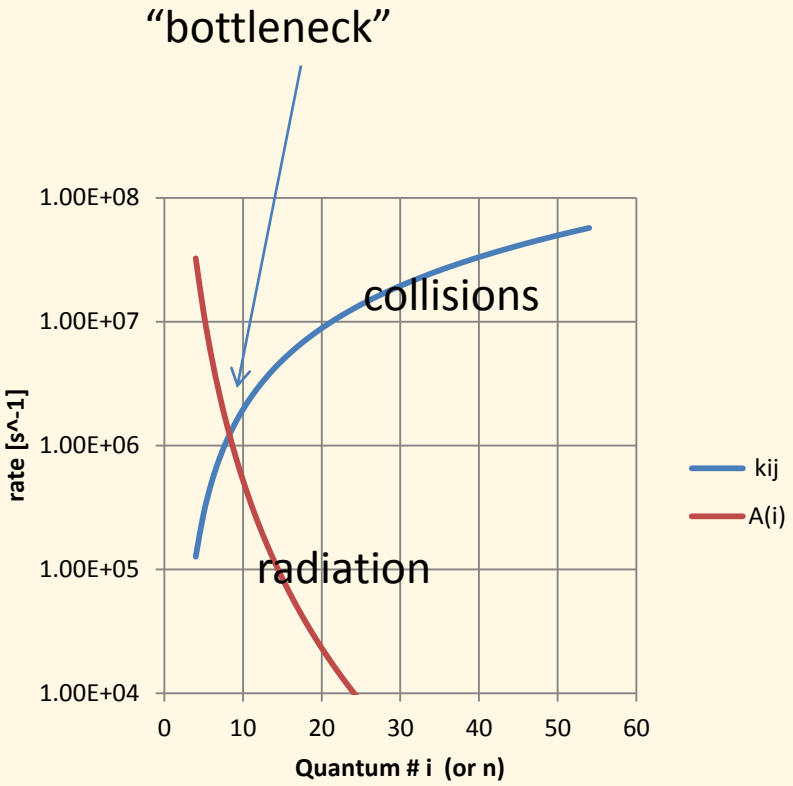
Conditions in this experiment



There must be something in the afterglow that prevents CRR

Energy release by CRR.





$n_e = 10^{11}$

T_e =77 K

Energy released per recombined ion:
Ionization potential of the state corresponding to the bottleneck

Here: n~ 8, corresponding to ~ 13.6/ 64 ~ 0.2 eV

Electron heating and cooling in CRR recombination.

U= internal energy of the electron gas

Energy released per recombined ion

Heat input from CRR

$$\frac{dU_{CRR}}{dt} = 3.8\times10^{-9} T_e^{-9/2} \quad n_e^3 \, \delta E \;\; [eVs^{-1}cm^{-3}]$$

Heat transfer to ions

$$\frac{dU_{e-ion}}{dt} = -3.2\times10^{-9} \; n_e^2 \, \frac{\lambda}{m_{ion}} (kT_e)^{3/2} (\frac{3}{2} kT_e - \frac{3}{2} kT_{ion})$$

$$\lambda = 23 - \ln[n_e^{1/2} (kT_e)^{3/2}] \quad \text{(Coulomb logarithm)}$$

Heat transfer to neutrals

$$\frac{dU_{e-gas}}{dt} = -n_e \, f_{coll} \, \frac{2m_e}{m_{gas}} (\frac{3}{2} kT_e - \frac{3}{2} kT_{ion})$$

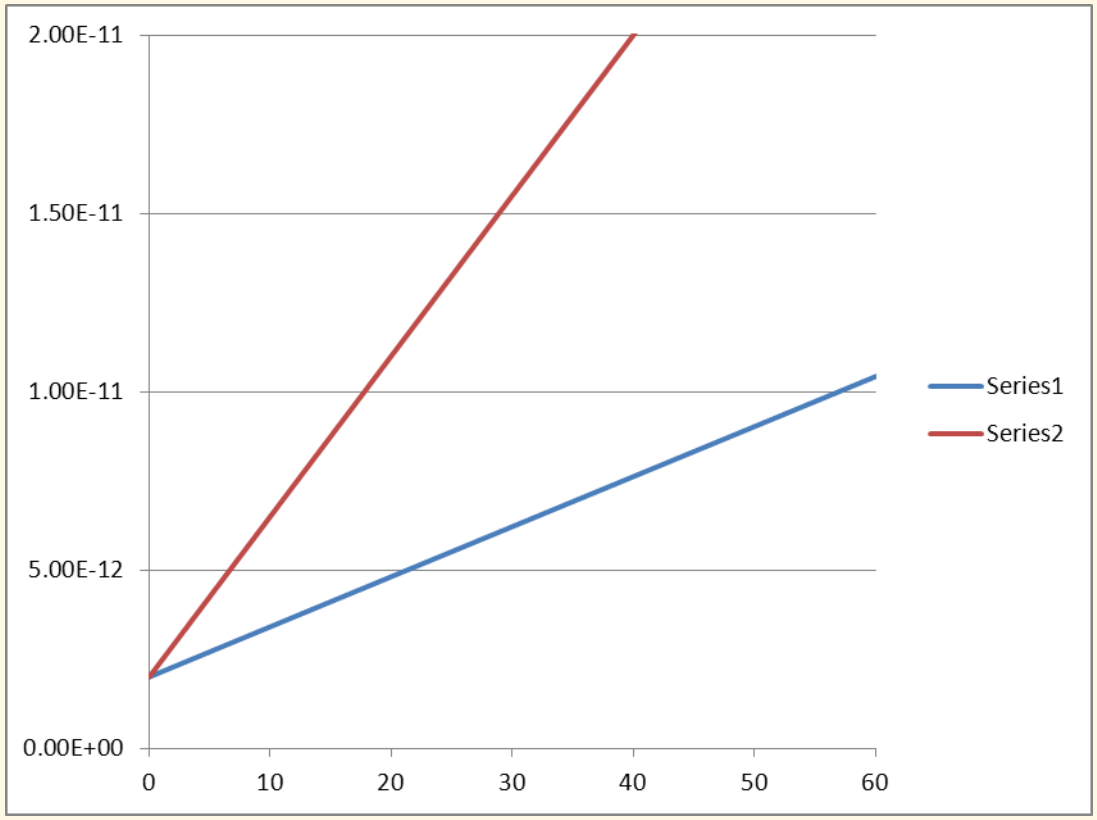
$$f_{coll} = e - gas \; collision \; frequency$$

In steady state : heat input=heat loss

NRL PLASMA FORMULARY

This is what one gets for CRR with heating but without H5+ formation.
It looks “binary” even though it is due to CRR.
The effect has been known for nearly 50 years

energy release		0.2eV	
T_gas		77K	
ne	Te		alpha_CRR
5.00E+11	178		1.42E-07
3.00E+11	158		1.41E-07
1.00E+11	124		1.44E-07
5.00E+10	107		1.40E-07
1.00E+10	84		8.33E-08



We need something else to explain the data, namely a small addition of H5+ in equilibrium with H3+. What is it? Destruction of H5+ by vibrationally hot H2?

In a stationary afterglow in H2, there will be long-lived vibrationally excited H2.

The reaction

$$H_3^+ + H_2 + H_2 \leftrightarrow H_5^+ + H_2$$

will approach an equilibrium at a temperature above the gas temperature.

The measured decay rate is due to combined H5+ H3+ recombination.
It again will look like binary recombination.

H2 vib will further increase the electron temperature

I can't make a quantitative model because I don't know the vibrational temperature

Conclusion: Studies in pure H_2 stationary afterglows are useful.
But they give effective recombination coefficients, not binary coefficients.

I don’t have the time to go into details of spectroscopic measurements in H2 afterglows

Work by Miderski and Gellene and by Amano showed that H3 and D3 are formed with excess kinetic energy.
The authors concluded that are produced by dissociative recombination

$H_5^+ + e^- \rightarrow H_3 + H_2$ + kinetic energy

I agree, but add that this process also accounts for the observed recombination loss

Direct “intervention” in the DR of H3+ by third bodies, helium in particular

The very extensive studies by the Prague group leave little doubt that the presence of helium in the afterglow enhances recombination

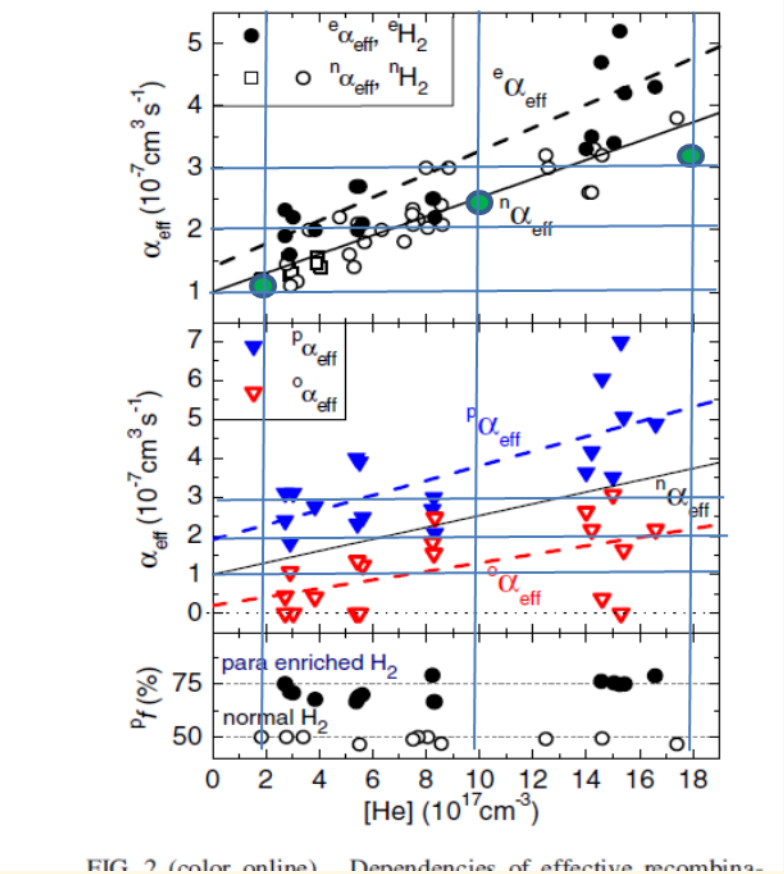


FIG. 2 (color online). Dependencies of effective recombina-

Helium has little effect on the ion composition of the plasma

Apparently, it changes H3+ Rydberg states by mixing angular momentum quantum numbers.

Only approximate models are available

Quantitative model of collisional dissociative recombination with l-mixing:

High Rydbergs (n>12) are formed very fast by three-body capture:

$$e^- + H_3^+ + M \leftrightarrow H_3^*(n,l) + M$$

Their concentration is estimated from the Saha equilibrium

$$\frac{[H_3^*(n)]}{[H_3^+]n_e} = K(n) = n^2 \lambda_{th}^3 e^{E_n/kT} \qquad \lambda_{th} = (h^2 / (2\pi m_e kT)^{1/2}$$

Irreversible destruction of these states enhances the recombination rate coefficient by:

$$\Delta\alpha = \sum_{n_{\min}}^{n_{\max}} K(n)\nu_s(n)$$

Irreversible destruction involves:

- *l*-mixing, either by electrons or atoms, into low l-states that predissociate
- Chemical reactions with neutral molecules (H2)

l-mixing rates

By electrons: $$k_{mix,e} = v_e 4.4 \times \pi a_0^2 n^5 [cm^3 / s]$$

Dutta, S.K., Feldbaum, D., Walz-Flannigan, A., Guest, J.R. and Raithel, G. 2001, "High-angular-momentum states in cold Rydberg gases", *Physical Review Letters,* vol. 86, no. 18, pp. 3993-3996.

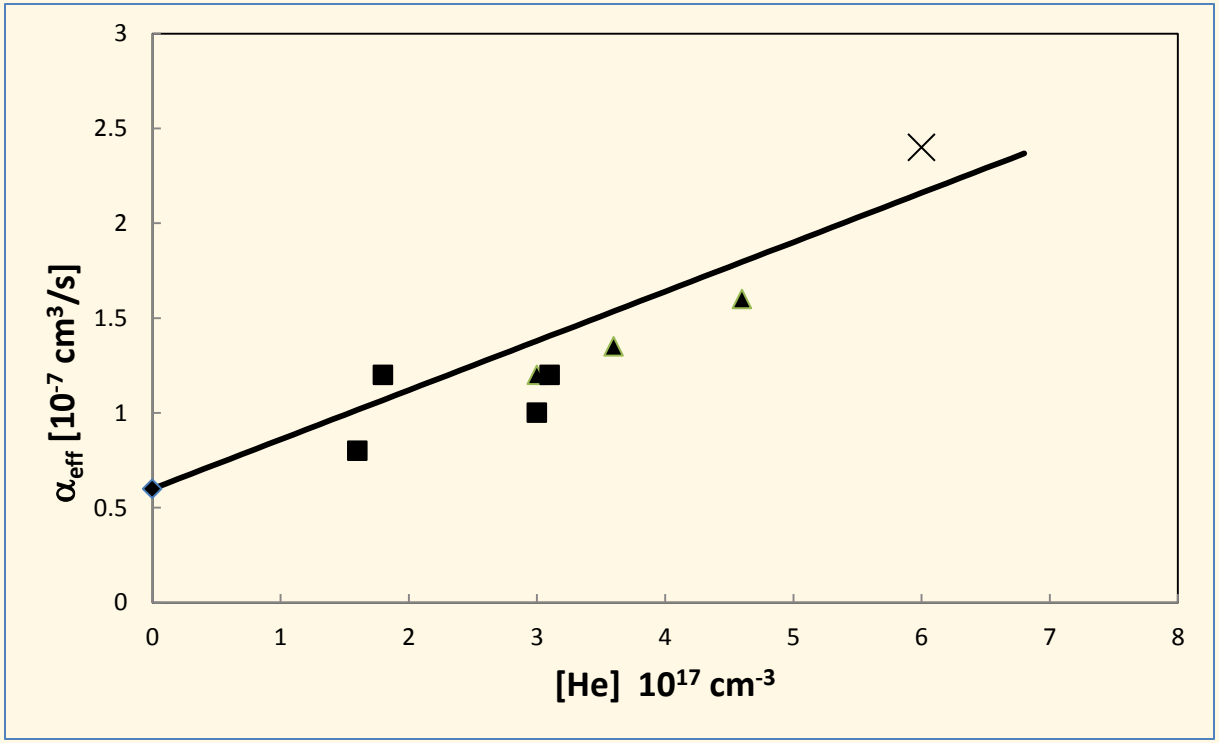
By helium: $$k_{mix,He} = 3.1 \times 10^{-5} \frac{1}{n^{2.7}} [cm^3 / s]$$

Hickman, A.P. 1978, "Theory of angular momentum mixing in Rydberg-atom-rare-gas collisions", *Physical Review A,* vol. 18, no. 4, pp. 1339-1342.

Note:
The rates are for *l*-mixing from a given *l* to any other *l'.*
The rates from a given l to a particular l' other than l are smaller by 1(n^2-1)

$$k'_{e,mix} = v_e \sigma'_{e,mix}$$

Model *vs.* data



Observed dependence of the H_3^+ recombination coefficient at T=300 K on the experimental helium density. Squares and triangles; data from Glosik (2009). Cross: from Leu at al, 1973. The line indicates the density dependence expected from the model described in the text.

Model of Glosik…. Greene, Kookouline

Rotational capture of an electron, followed by l-mixing with helium, and eventual stabilization

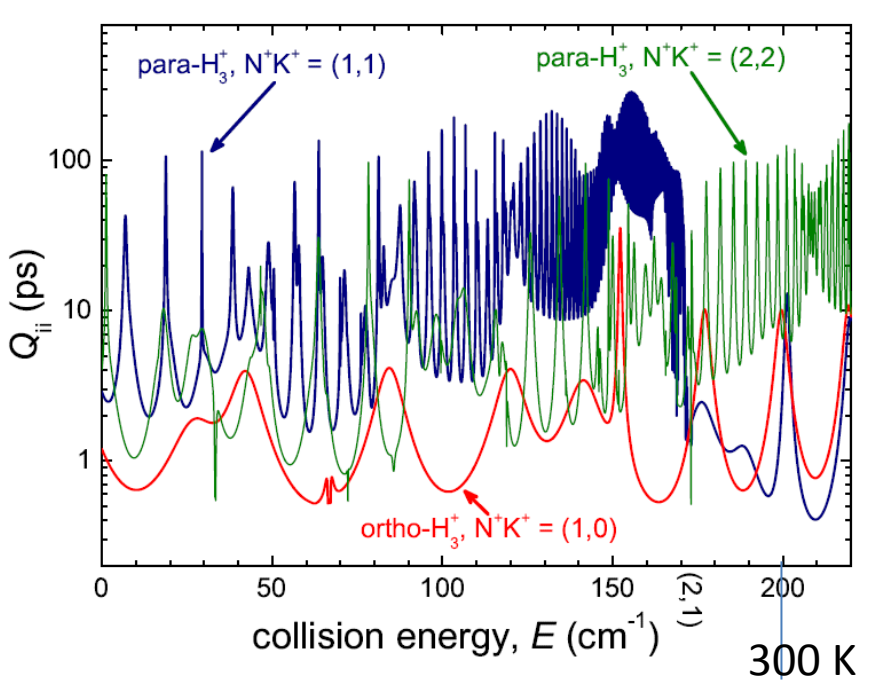


FIG. 8: Diagonal elements Q_{ii} of matrix Q for the three lowest (rotational) incident channels for the $e^- + H_3^+$ collisions. The rotational channels are $(N^+, K^+) = (11), (10),$ and (22). Each maximum in Q_{ii} corresponds to an autoionization resonance. The lifetime of a resonances is given by $Q_{ii}/4$ evaluated at the maximum if there is only one channel open, $Q_{ii} = Q$.

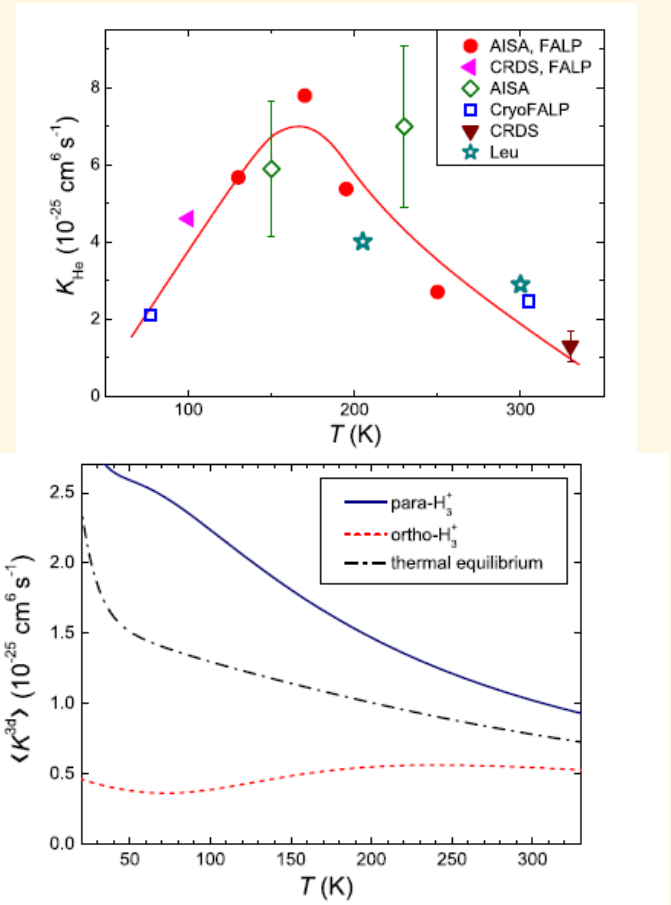
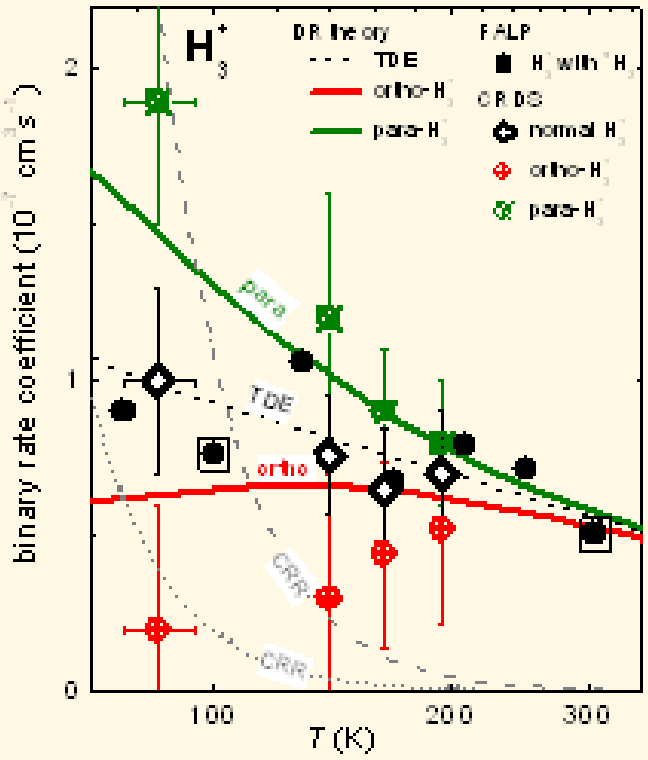


FIG. 9. (Color online) Calculated thermally-averaged three-body rate coefficient $\langle K^{3D} \rangle$. The rate coefficients calculated separately for ortho- and para-H_3^+ are very different. If the recombining plasma is not in thermal equilibrium with respect to ortho to para ratio, the averaged rate coefficient (dashed) could be very different from the one shown.

Model of Glosik…. Greene, Kookouline

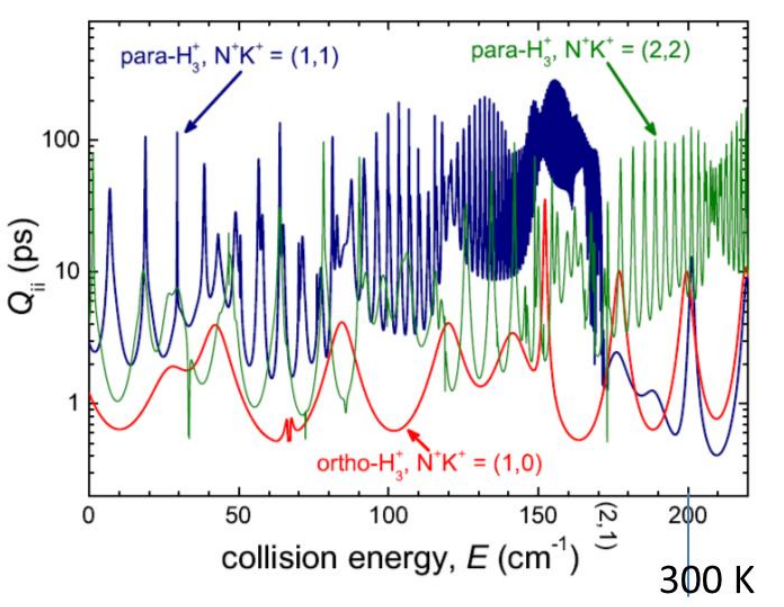
I like the first part (rotational capture), but the assumed l-mixing rate due to helium seems to be too large

Neither model can be expected to be accurate. More work is needed.

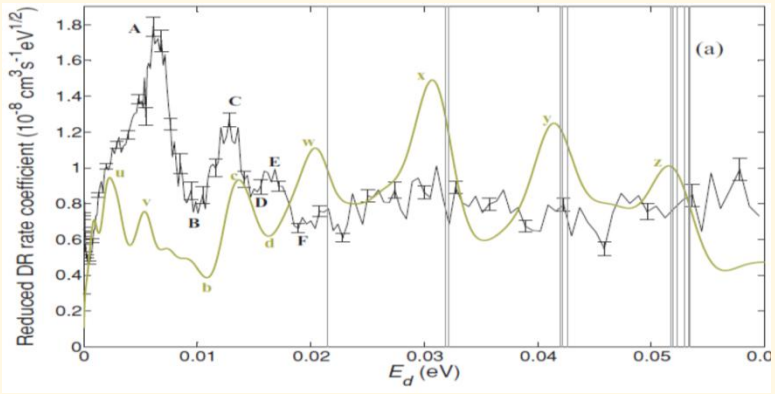

H3+
DR theory
TDE
ortho-H3
para-H3
FALP
H3 with H2
CRDS
normal H3
ortho-H3
para-H3
para
TDE
ortho
CRR
CRR
binary rate coefficient (10-7 cm3 s-1)
2
1
0
100
200
300
T (K)

A funny observation that may or may not mean anything

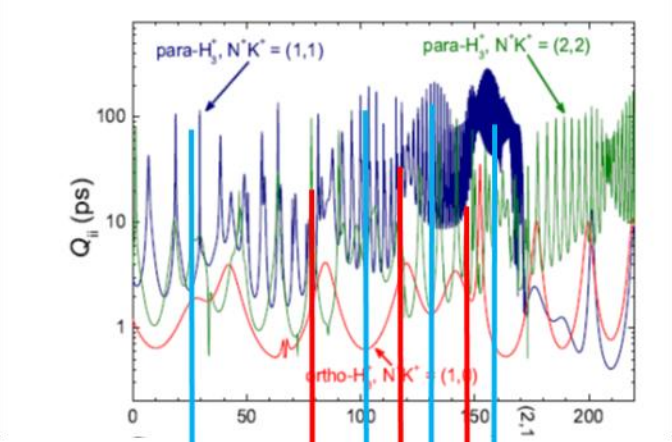
Join the lifetime graph for rotational resonances
[blue for paraH3+ (1,1) to (2,1)]

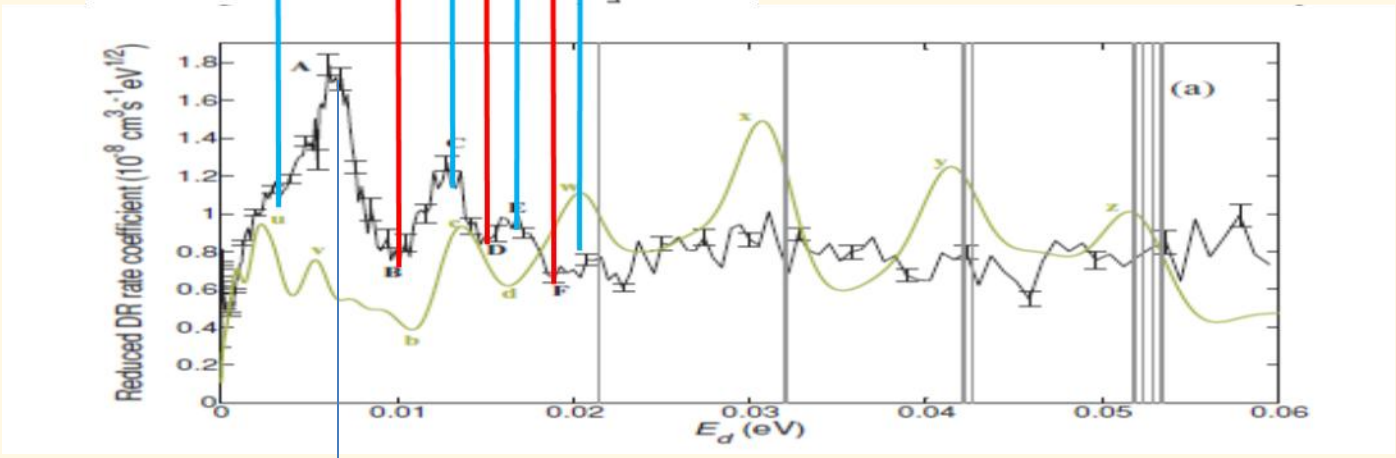


…and the low-energy structure of the storage-ring data



There seems to be a correlation between the peak positions





The “A” peak has no counterpart. It come from something else.

The “A” peak does not seem to change when para enriched H2 is used in the ISR

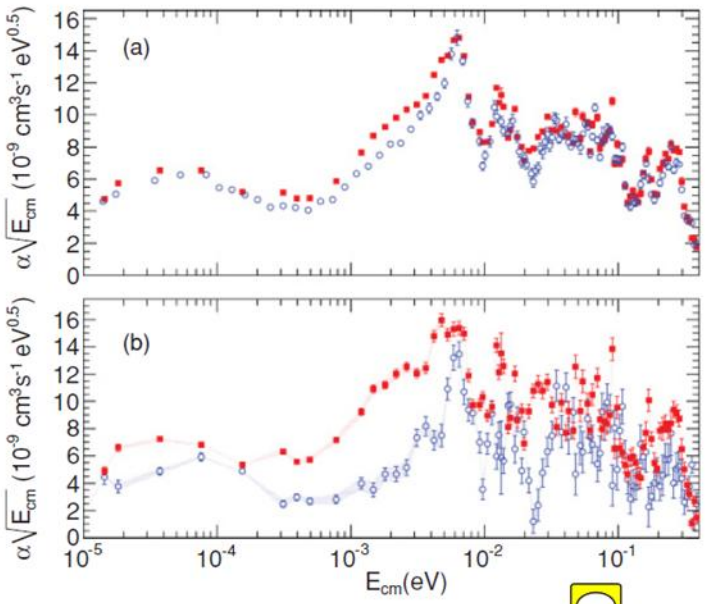
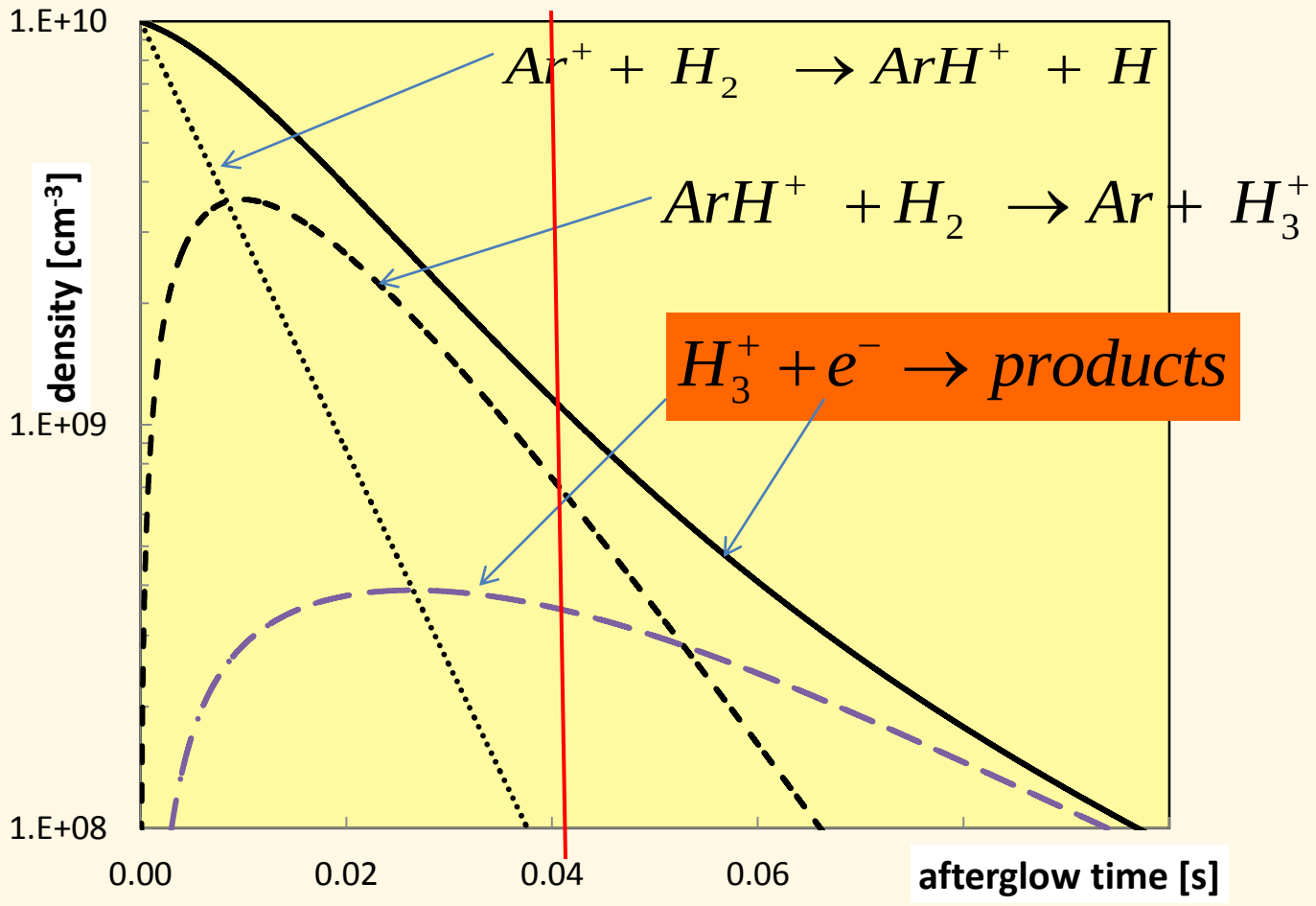


FIG. 8. (Color online) Comparison of the DR rate coefficient for different nuclear spin modifications of H_3^+. The upper panel (a) shows the results obtained with the supersonic expansion source and 1:5 n-H_2:Ar (blue circles) and 1:5 p-H_2:Ar (red squares) mixtures. The lower panel (b) shows the extrapolated results for “pure” p-H_3^+ (red squares) and “pure” o-H_3^+ (blue circles). For the extrapolation we assume a p-H_3^+ fraction of (47.9 ± 2)% for n-H_2:Ar and (70.8 ± 2)% for p-H_2:Ar (see discussion in the text). The error bands in the lower panel represent the effect of the 2% uncertainty in the spectroscopic determination of the p-H_3^+ fractions.

Even after 40ms afterglow time, the plasma contains mainly ArH+!



Numerical simulation of an afterglow in a helium/argon/hydrogen mixture at a hydrogen concentration of 1×10^{11} cm^{-3} for an assumed H_3^+ recombination coefficient of 1×10^{-7} cm^3/s. The lines indicate the evolution of density of electrons (thick line), of Ar^+ ions (dotted line, ArH^+ ions (dashed line), and H_3^+ ions (dash-dotted line).