Kinetic Processes in Recombining H_3^+ plasmas

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THEO MURPHY INTERNATIONAL SCIENTIFIC MEETING ON
Chemistry, astronomy and physics of H_3^+
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See also my poster:
"Old and new recombination and spectroscopic studies in H_3^+ afterglows"

Why does H_3^+ recombine faster in afterglows than in storage rings (theory)?

- Neutral assisted three-body recombination? Mechanism?
- Collisional radiative recombination?
- Presence of H_5^+ ?

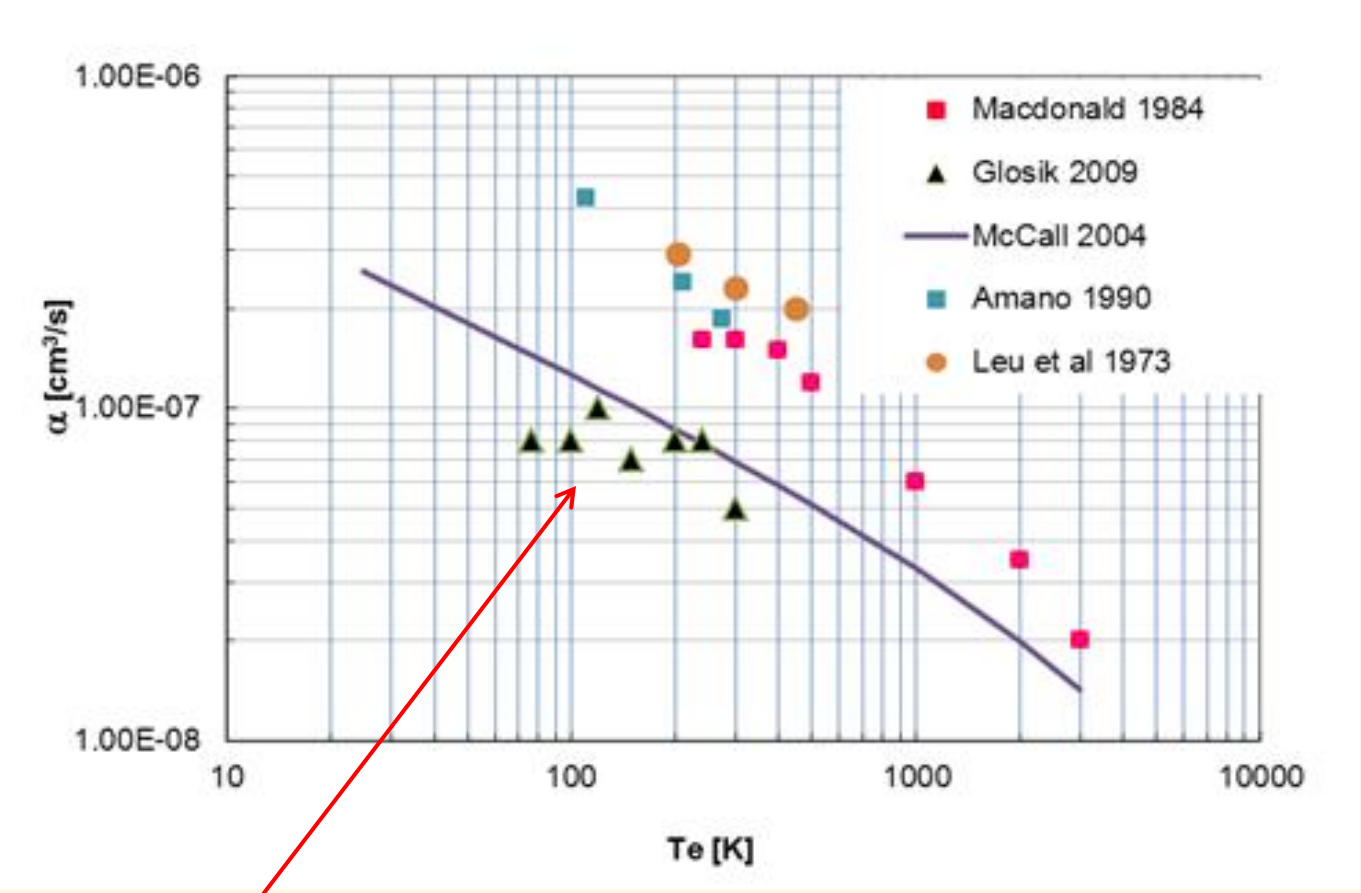
What is the source of H_3 (D_3)emissions in discharges/afterglows?

- Dabrowski & Herzberg: H_3^+ recombination (Coll. Rad. ?)
- Miderski an Gellene: $H_5^+ + e^- \rightarrow H_3^* + H_2$ (line broadening)
- Amano (D_2 plasmas): $D_5^+ + e^- \rightarrow D_3^* + D_2$ (some lines broadened, some not)

How does it all fit together?

A quick look at a few afterglow studies.

H_3^+ ions recombine faster in afterglows than in storage rings, more so at low temperatures.



Corrected for three-body recombination

An important study that changed the history of H_3^+ recombination.
Amano: Afterglow of a hollow cathode discharge in pure $[H_2]$~ $5x10^{16}$ cm-3
Monitored decay of $H_3^+(v=1)$ by optical absorption

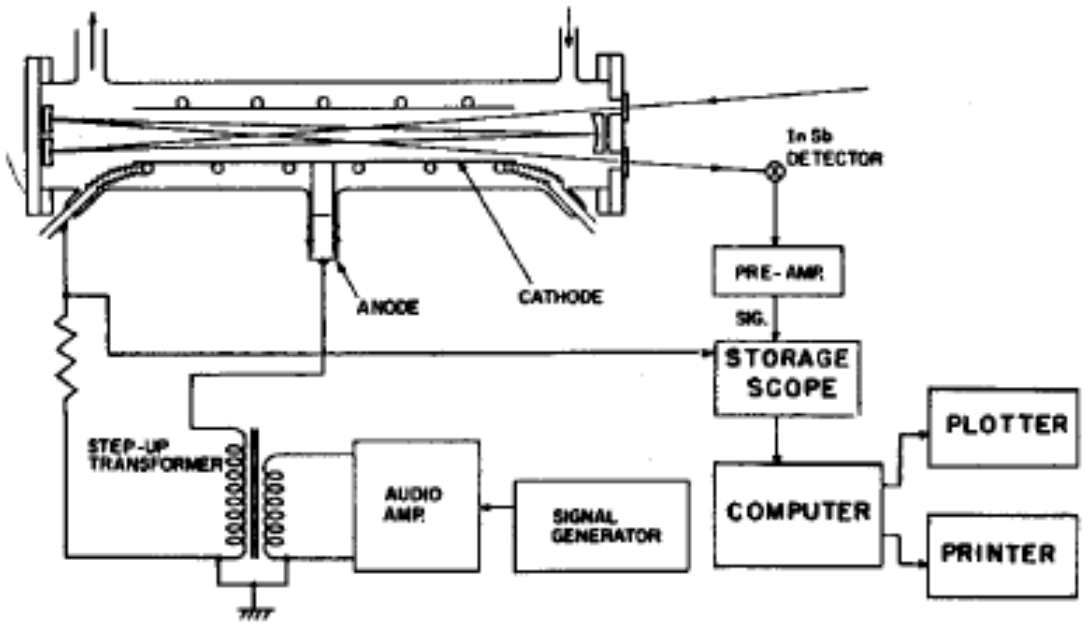


FIG. 1. A schematic diagram of the spectrometer system.

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

6492 J. Chem. Phys. **92** (11), 1 June 1990

Amano's recombination plot looks perfect. Compatible with binary recombination
Conclusion: α(110 K)~4.3x10^{-7} cm^3/s

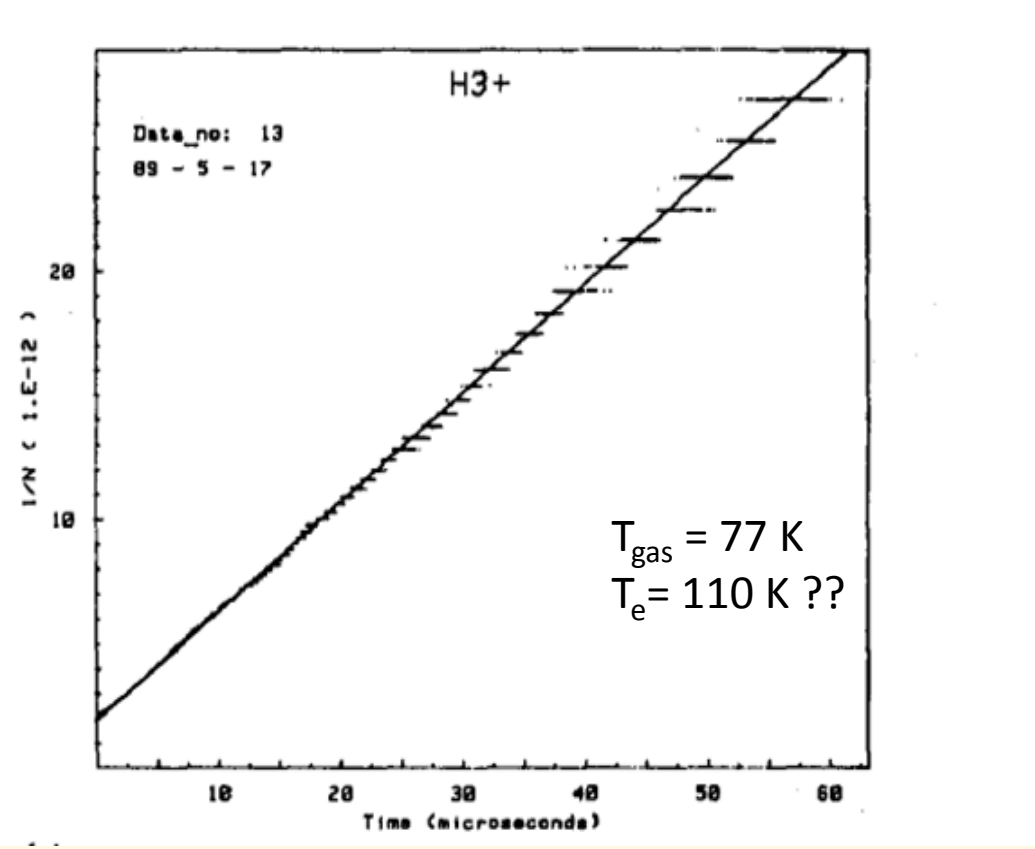


TABLE I. The dissociative recombination rate coefficients of H_3^+ in the ground vibrational state (in units of 10^{-7} cm^3 s^{-1}).

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)

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

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(Received 24 August 1989; accepted 23 February 1990)

Note: High initial n_e= 5x10^{11} cm^{-3}

But:

1. The H_3^+ ions should have converted to H_5^+ (which recombines 20 times faster!)

2. Collisional radiative recombination (CRR) should have been a big effect

First problem

At 77 K the reaction:

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

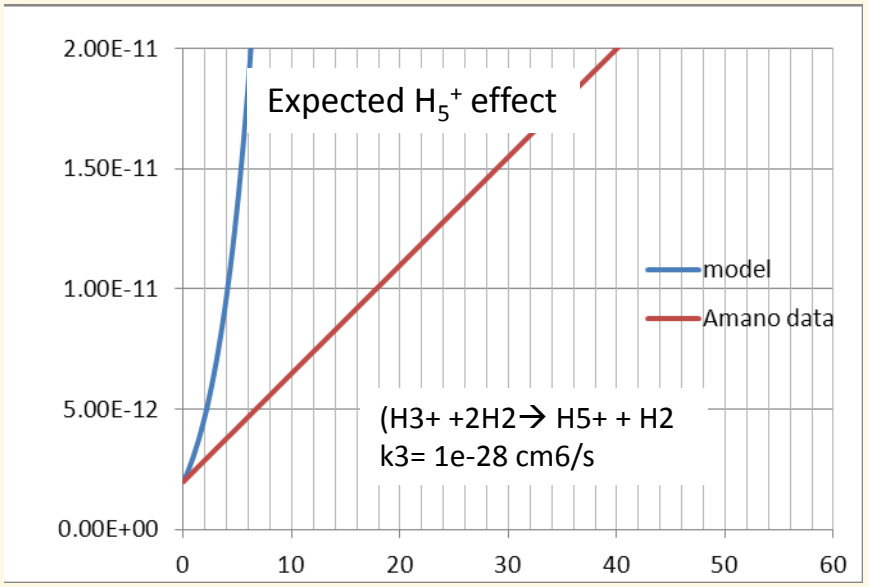
is fast!

It's inverse

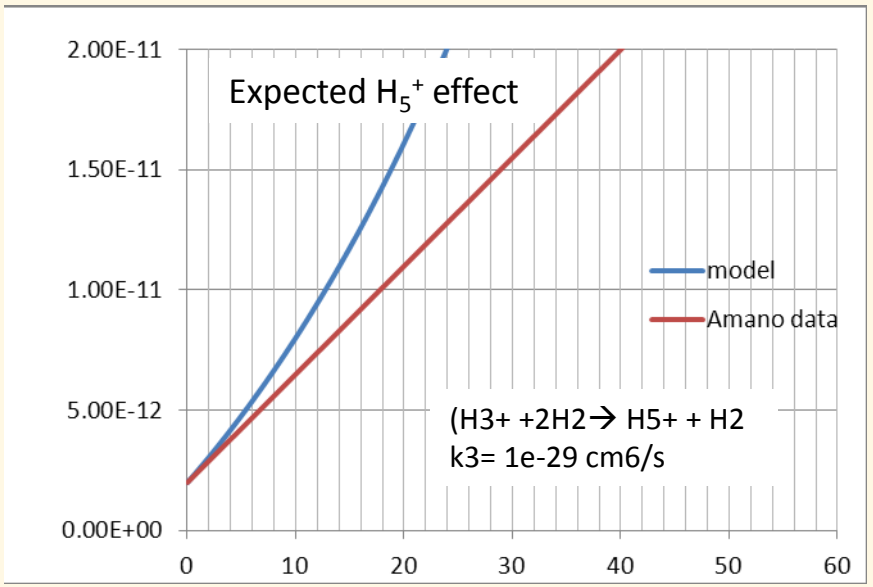
$$H_5^+ + H_2 \rightarrow H_3^+ + H_2 + H_2$$

is slow!

Something must have broken up H_5^+ !?



This uses the rate of Hiraoka & Kebarle

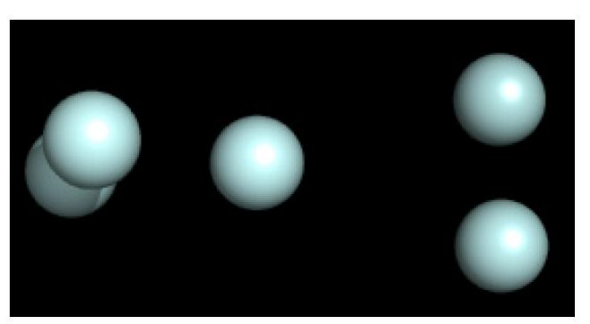


This uses 10% of the rate of Hiraoka & Kebarle

Tentative answer:
The plasma contained <u>vibrationally excited H_2</u>

H_5^+ is a weakly bound ion.
Binding energy ~ 0.35 eV

$$H_5^+ + H_2(vib) \rightarrow H_3^+ + H_2 + H_2$$



The reaction

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

equilibrates, but at a temperature higher than the kinetic temperature

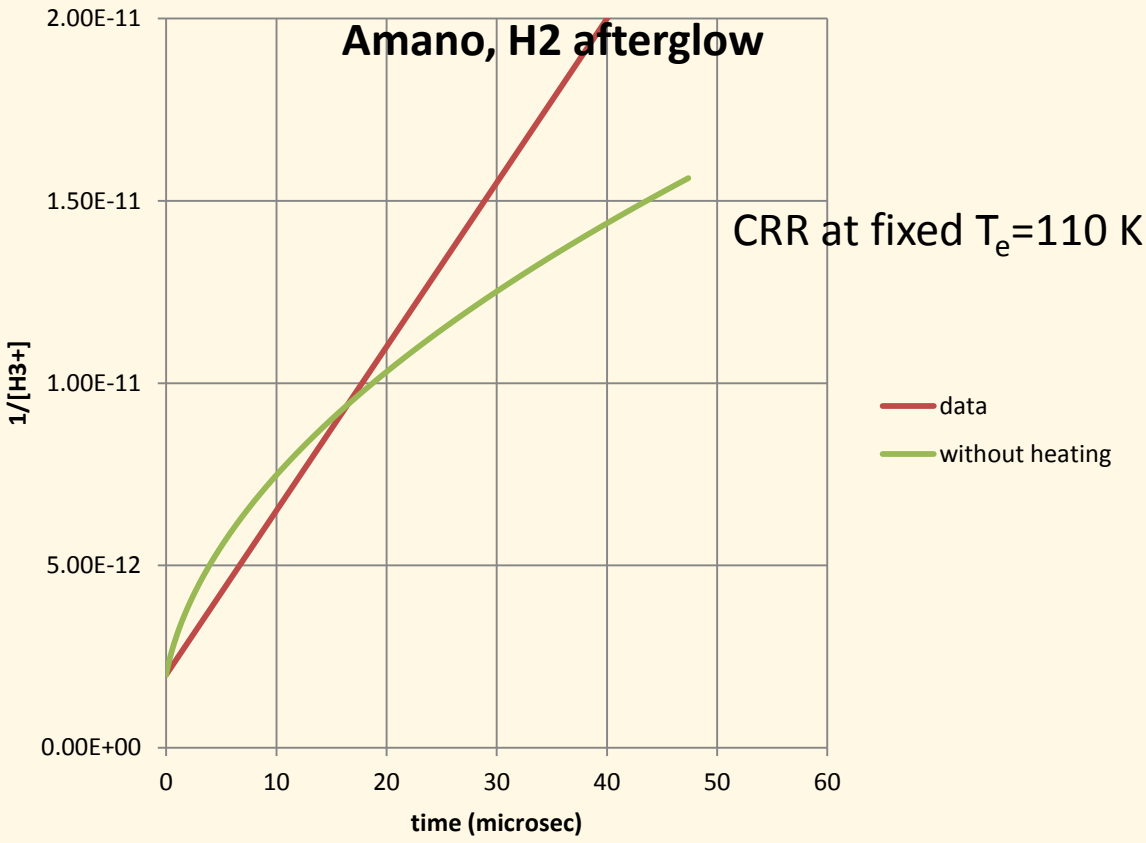
The recombination coefficient for the mixture

$$\alpha_{eff} = f_3\alpha(H_3^+) + f_5\alpha(H_5^+)$$
$$f_3 + f_5 = 1$$

is much higher!
f_5=4% would double the rate!

Second problem

CRR should have had a big effect. Why did it not?



CRR at fixed T_e=110 K

The “Stevefelt* formula” gives the “effective binary” CRR rate coefficient as:

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

collisions

radiation

correction term

At low T_e and high n_e, the first term dominates.

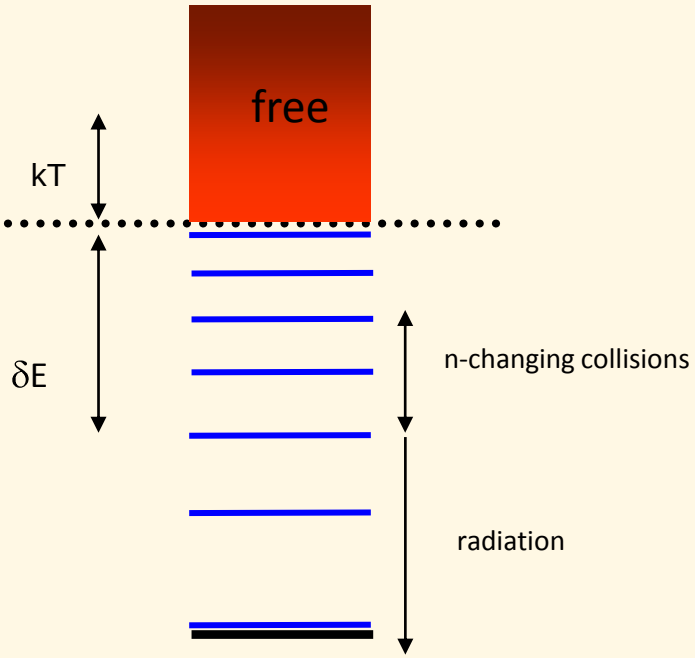
Looks very simple!

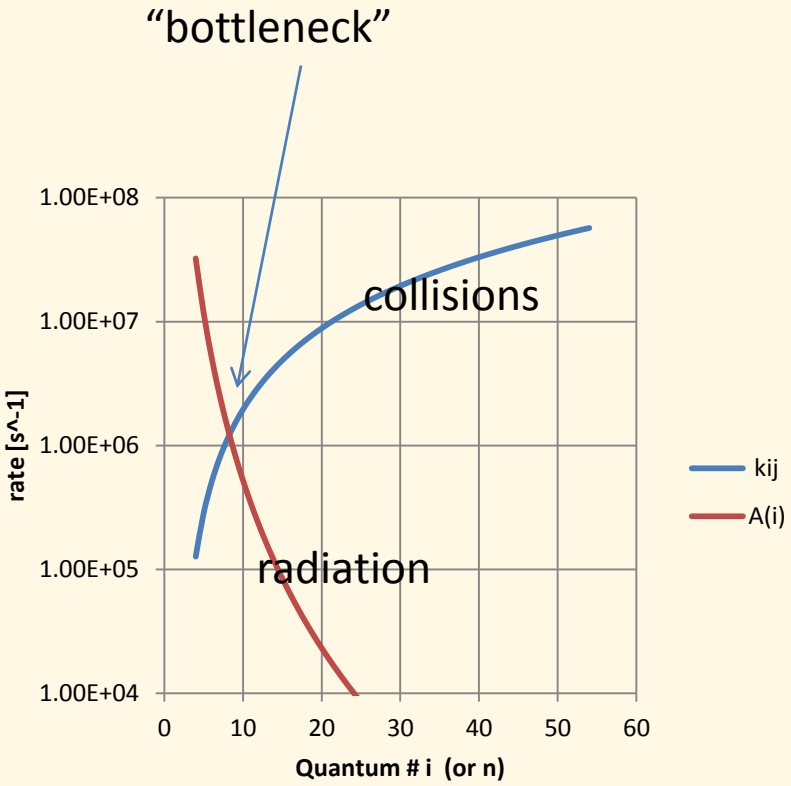
<u>But the electron temperature is not really an independent, known variable!</u>

(Bates, Byron et al pointed this out long time ago)

* J. Stevefelt, J. Boulmer, and J-F. Delpech, Phys. Rev. A **12**, 1246 (1975)

CRR heats the electron gas





$n_e = 10^{11}$

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

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

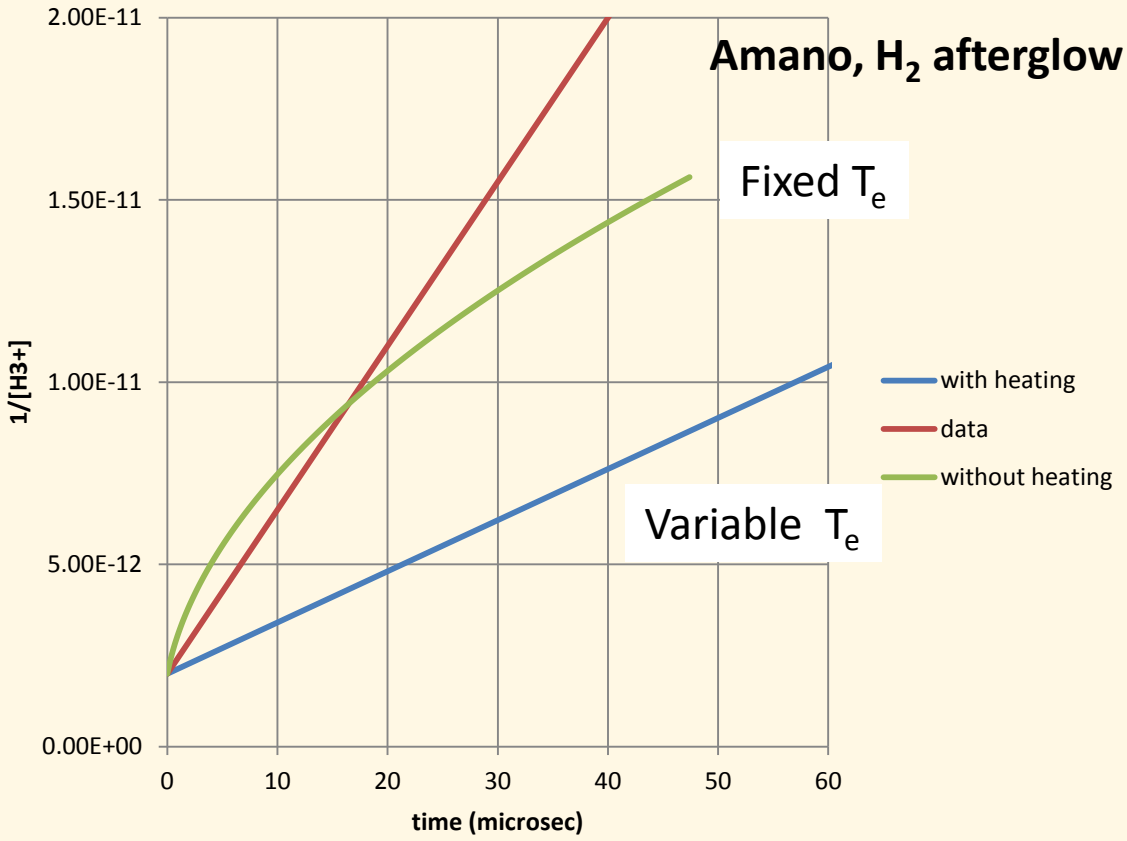
$$f_{coll} = e - gas \; collision \; frequency$$

In steady state : heat input=heat loss

NRL PLASMA FORMULARY

If one takes the heating into account, CRR looks “binary”

The rate-limit is the rate of “electron cooling” in electron-ion collisions
The electrons must cool before they can recombine!



Conclusion 1:

- Recombination in a low-temperature (~100 K) pure H_2 afterglow (n_e> ~10^{11}occurs mainly by CRR and H_5^+ recombination.

- The experiments don't prove or disprove that H_3^+ binary recombination is "fast".

- The H_3 emission and absorption spectra most like arise from CRR and H_5^+

This largely agrees with the conclusion drawn from spectroscopic observations.
Two quotes from Amano and Chan (2000)*

> The next question is how the line shapes and their rotational dependence are to be understood. We assume that D_3 is supplied to each state through two distinct paths:
> *a direct supply from the dissociative recombination of D_5^+ and a cascade from the upper states*. The molecules cascaded down from the upper states have less kinetic energy, resulting in smaller Doppler widths.

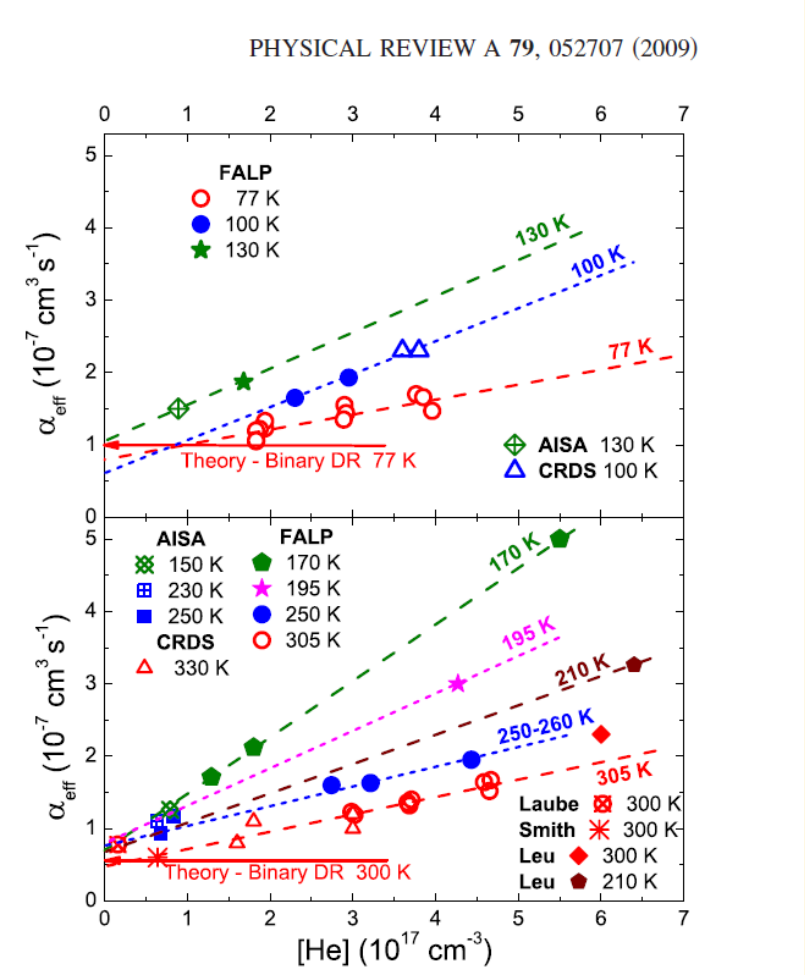
But they had some doubts:

> We found that no substantial increase of the absorption intensity was achieved at liquid nitrogen temperature. If the formation process is the dissociative recombination of D_5^+, a much more conspicuous temperature dependence is likely to show up.

* Amano, T. and Chan, M-C. (2000) Infrared absorption spectroscopy of D_3: an investigation into the formation mechanism of triatomic hydrogenic species *Phil. Trans. R. Soc. Lond. A***358**, 2457-2470

Afterglows in mixtures of He, Ar, and H_2
Very extensive data from the Prague group

Recombination is enhanced by helium.
The binary recombination coefficient is obtained from the [He] → 0 limit




PHYSICAL REVIEW A 79, 052707 (2009)

Temperature dependence of binary and ternary recombination of H_3^+ ions with electrons

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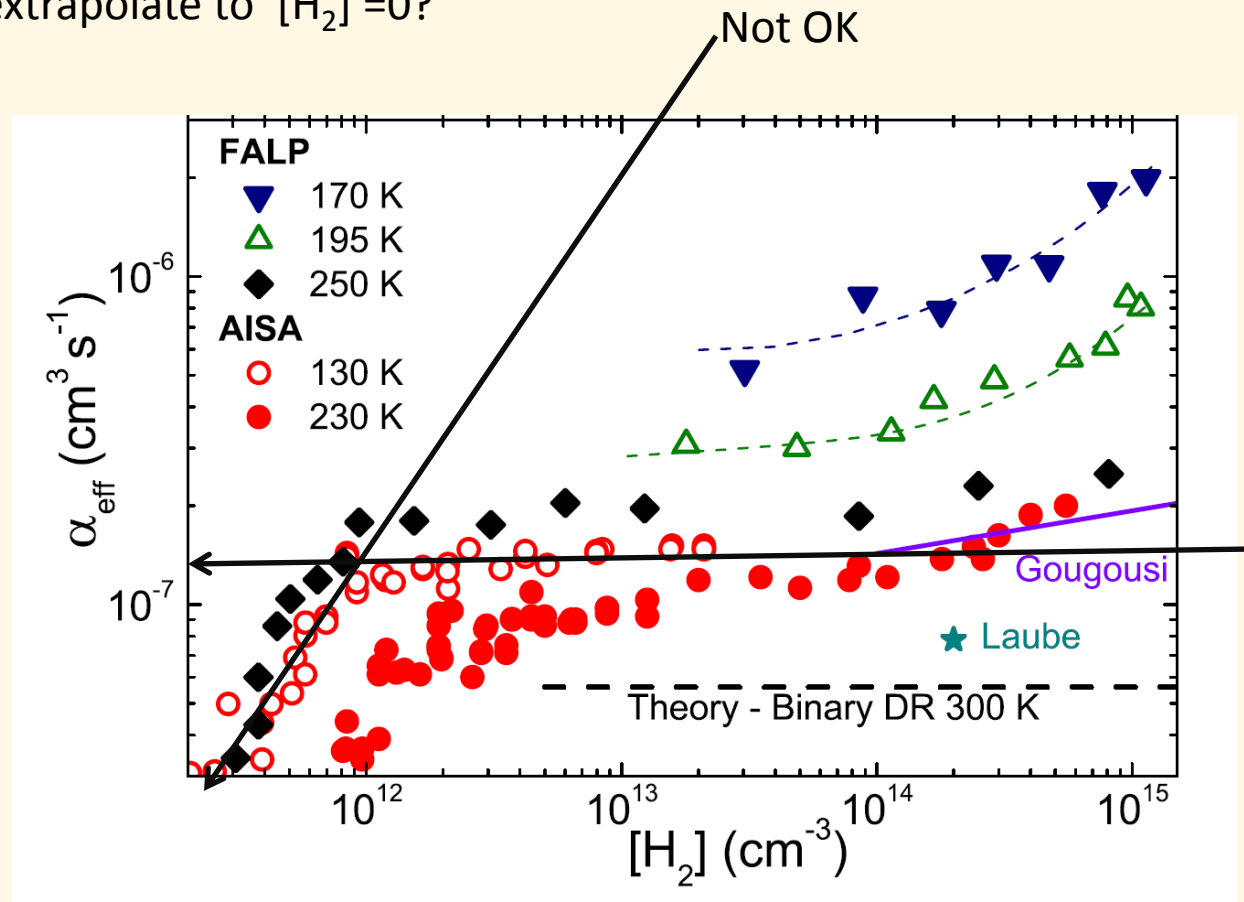
(Received 9 March 2009; published 26 May 2009)

Why not extrapolate to $[H_2]$ =0?



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

The H_3^+ formation becomes <u>rate-limiting</u>!

$Ar^+ + H_2 \rightarrow ArH^+ + H$ and $ArH^+ + H_2 \rightarrow Ar + H_3^+$ (10^{-9} cm^3/s) will take ~ <u>10 msec</u> at $[H_2] = 10^{11}$ cm^{-3}

Recombination of an ion with $\alpha = 10^{-7}$ cm^3/s (at $n_e = 10^{10}$ cm^{-3}) takes time $1/(\alpha\, n_e)$=<u>1 msec</u>.
(It would work if α actually were much smaller but does not rule out $\alpha = 10^{-7}$ cm^3/s)

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

much faster than it is lost by recombination.

Otherwise, H_3^+ is not the dominant ions

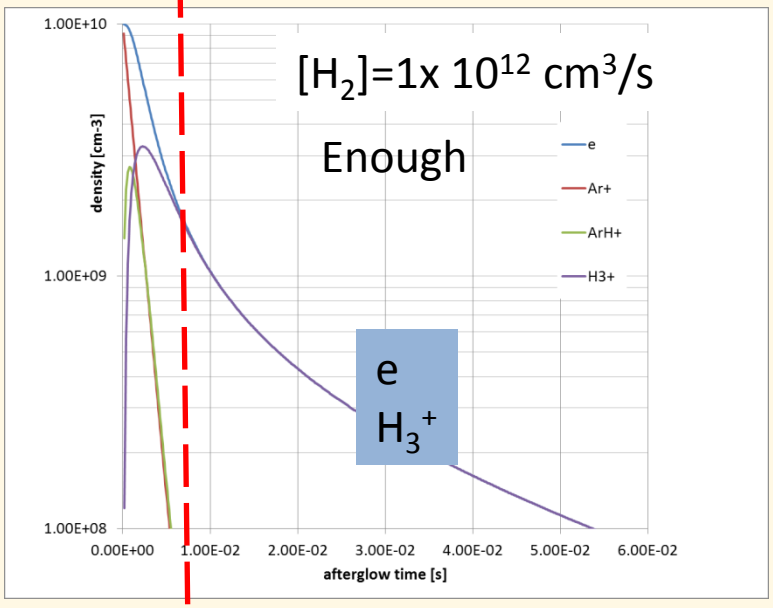
Production:

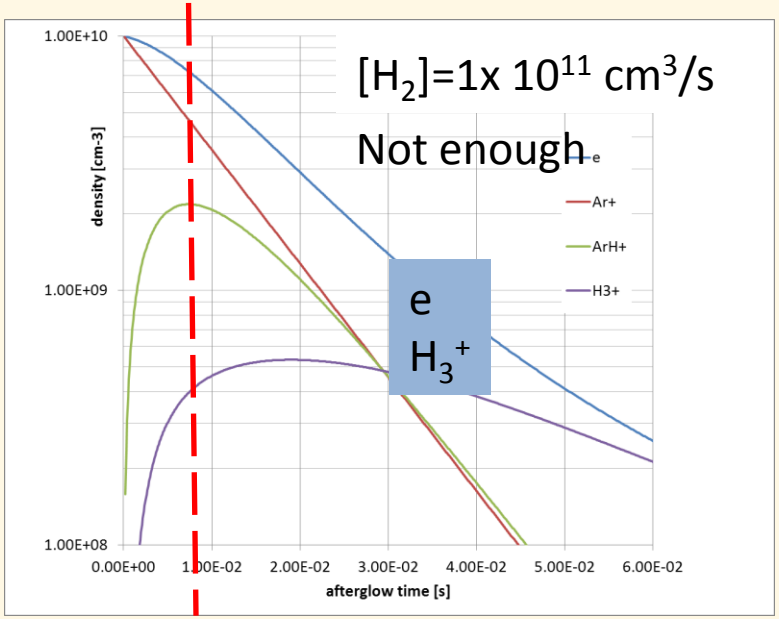
$$Ar^+ + H_2 \rightarrow ArH^+ + H$$

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

Loss:

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





Conclusion 2

1. There is good evidence for the dependence $\alpha(H_3^+)$ on [He]

2. But not for a dependence of $\alpha(H_3^+)$* on $[H_2]$ below 10^{12} cm^{-3}**

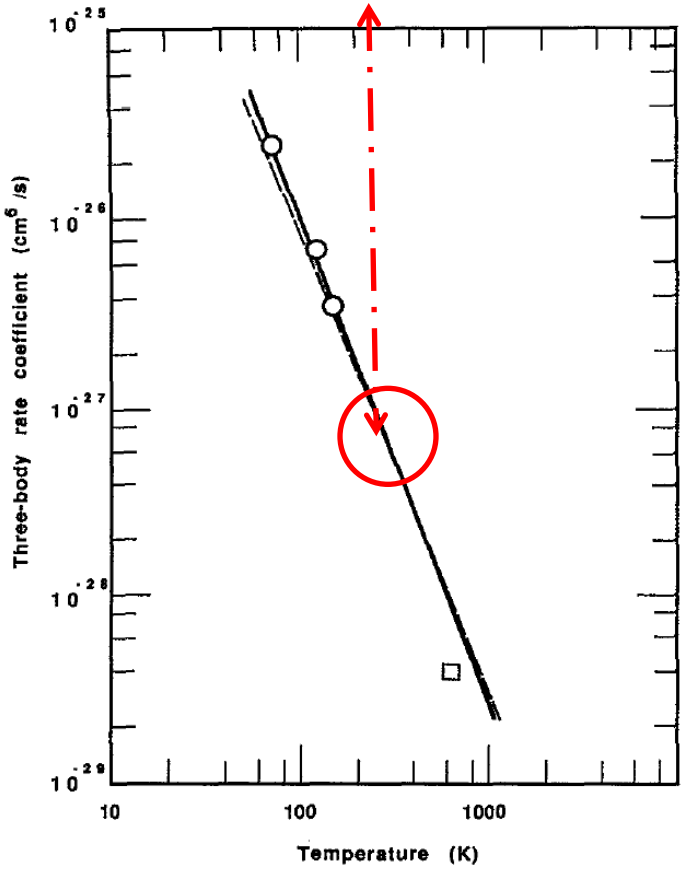
Notes:

- Possible loophole: H_3^+ para/ortho ratio depends on $[H_2]$, and para and ortho recombine with different rates (not likely at 300 K)

** This does not exclude a possible dependence of $\alpha(H_3^+)$ on $[H_2]$ at higher densities

How do we explain the dependence on [He]?

The “classical” neutral-stabilized mechanism is too slow



- Energy transfer in e- He collision is inefficient.
- Momentum transfer is more efficient

- Look at angular momentum mixing
  “l-mixing”

Neutral-stabilized electron–ion recombination in ambient helium gas

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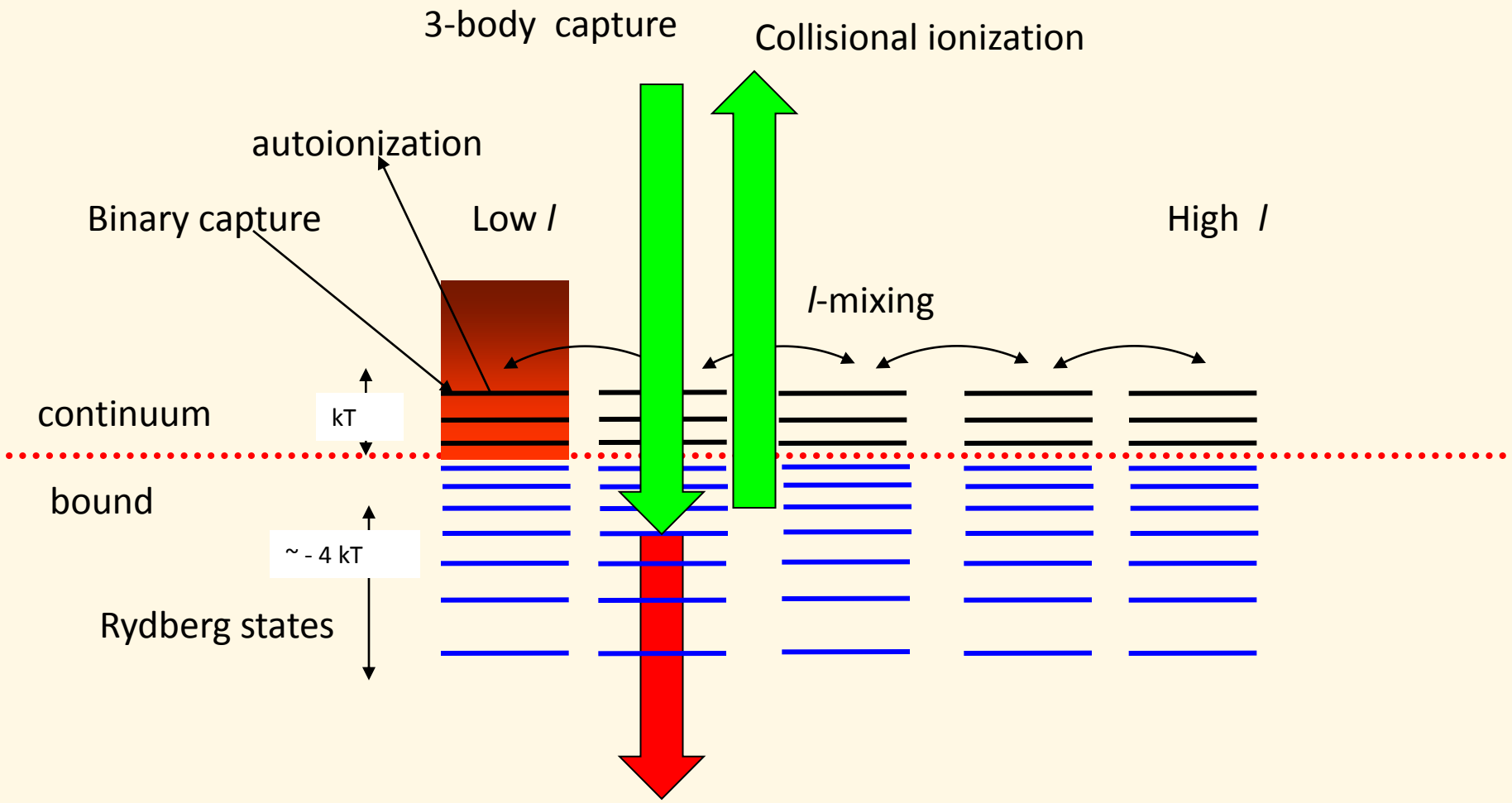
(Received 7 November 1990; accepted 31 December 1990)

J. Chem. Phys., Vol. 94, No. 8, 15 April 1991

Third-body- assisted recombination mechanisms



Third-body effects can enhance recombination only if they stabilize states that can still be re-ionized. (by collisions or autoionization)
At low temperatures, low n states cannot be ionized and their stabilization by third bodies is not effective

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.

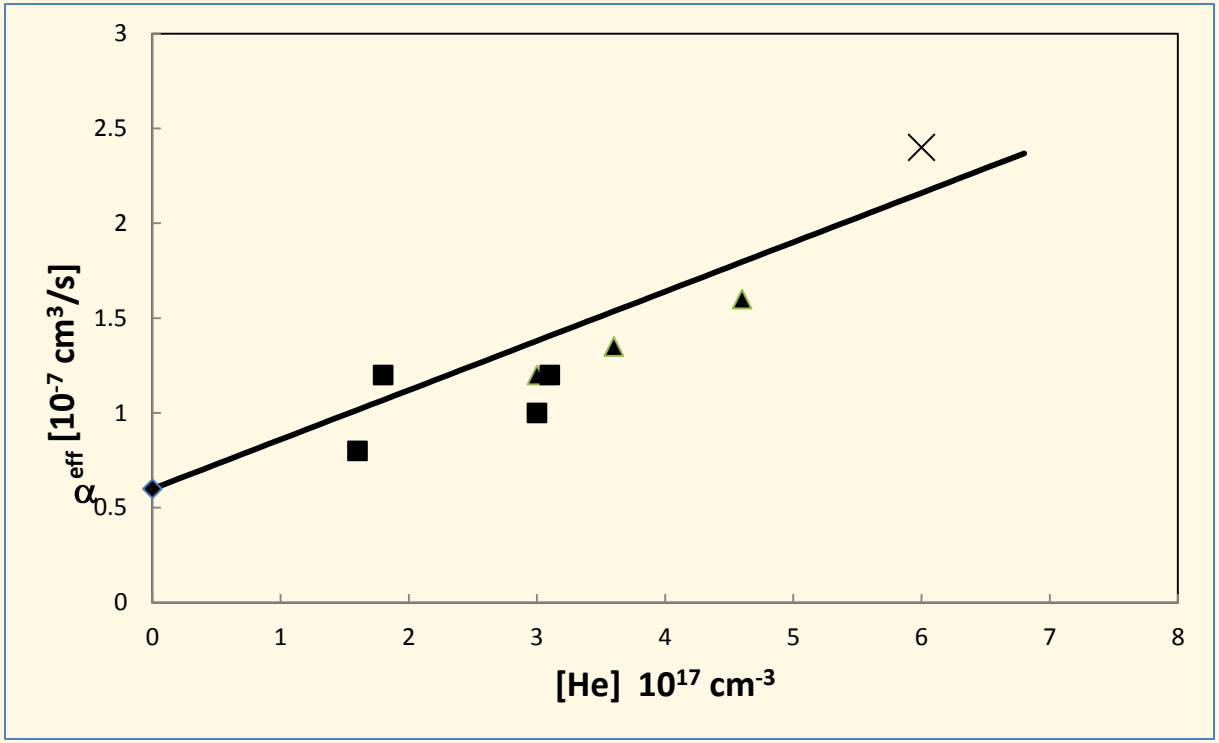
By helium: $$k_{mix,He} = 3.1 \times 10^{-5} \frac{1}{n^{2.7}} [cm^3 / s]$$

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

$$rotational\ \ capture$$

$$H_3^+ + e^- \rightleftarrows H_3^*(p,n)$$

$$l - mixing$$

$$H_3^*(p,n) + He \rightarrow H_3^*(l,n) + He$$

$$H_3^*(l,n) \rightarrow stabilized\ ??$$

He-assisted Model of Glosik…. Greene, Kookouline

Rotational capture of an electron into n>40 , followed by *l*-mixing with helium, and eventual stabilization

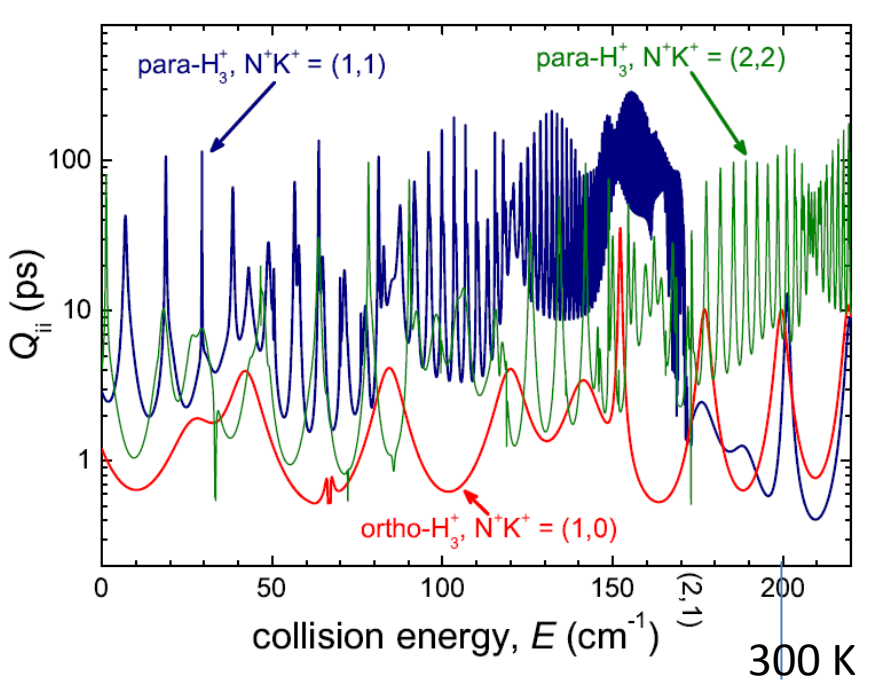
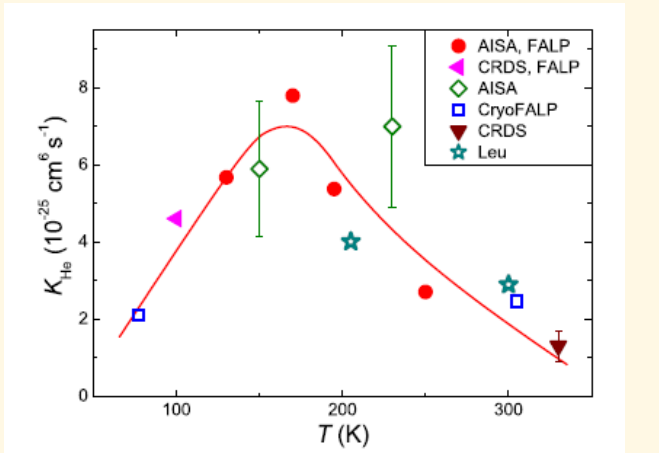


FIG. 8: Diagonal elements Q_{ii} of matrix Q for the three lowest (rotational) incident channels for the $e^- + H_3^+$ collisions. The rotational channels are $(N^+, K^+) = (11), (10),$ and (22). Each maximum in Q_{ii} corresponds to an autoionization resonance. The lifetime of a resonances is given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



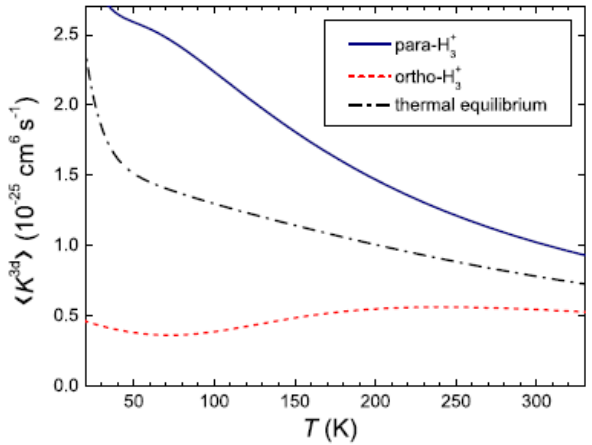


FIG. 9. (Color online) Calculated thermally-averaged three-body rate coefficient $\langle K^{3D} \rangle$. The rate coefficients calculated separately for ortho- and para-H_3^+ are very different. If the recombining plasma is not in thermal equilibrium with respect to ortho to para ratio, the averaged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

Comments on the Glosik et al He-assisted model

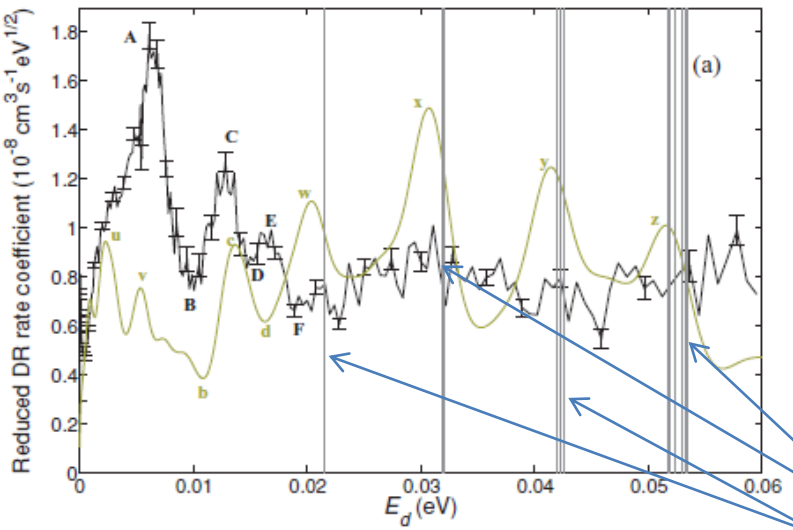
- The assumed *l*-mixing rates for high n (>40) are too large
- States with n>40 are in Saha equlibrium, no further *l*-mixing is needed

It may work for rotational capture into lower Rydberg states

But: It can contribute only if these resonances do not dissociate, as assumed

However, if they actually do dissociate, that should leave a trace in the storage-ring data. So, let's look

Low energy peaks in storage-ring data

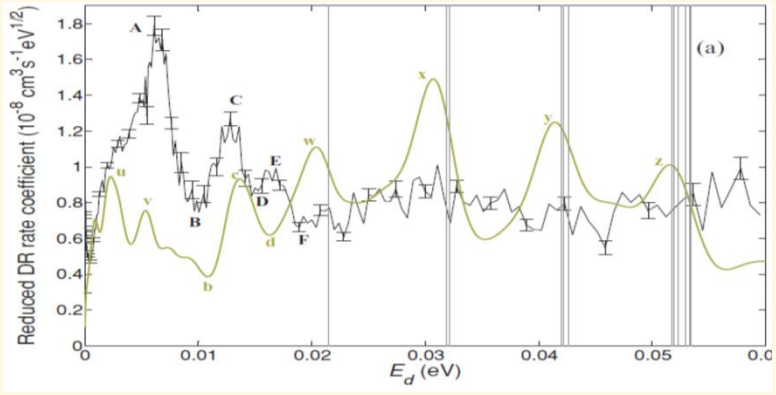


LE III. Ionization thresholds relevant to a *p*-wave electron ...g at low energy with the H_3^+ ion in different initial ionic energy eigenstates characterized by either ortho (A_2'' or A_2') or para (E'' or E') symmetry.

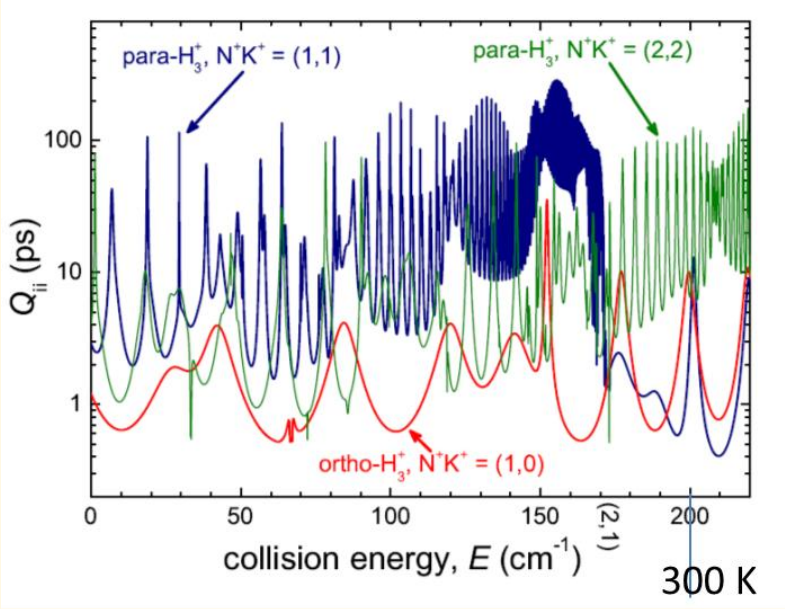
Target state (N^+,K^+)	Upper state	$E_{threshold}$ (meV)
E'' (1,1)	(2,1)	21.5
E'' (1,1)	(3,1)	53.4
E'' (2,1)	(3,1)	31.9
E'' (3,1)	(4,1)	42.0
E'' (4,1)	(5,1)	51.7
E' (2,2)	(3,2)	32.1
E' (3,2)	(4,2)	42.2
E' (4,2)	(5,2)	51.9
E' (4,4)	(5,4)	52.9
A_2' (1,0)	(3,0)	53.3
A_2'' (3,3)	(4,3)	42.6
A_2'' (4,3)	(5,3)	52.3

A. Petrignani et al , PHYSICAL REVIEW A 83, 032711 (2011)

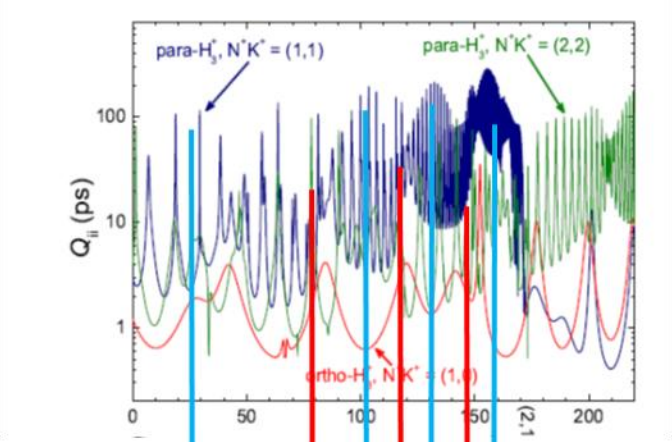
Low-energy structure
of the storage-ring data

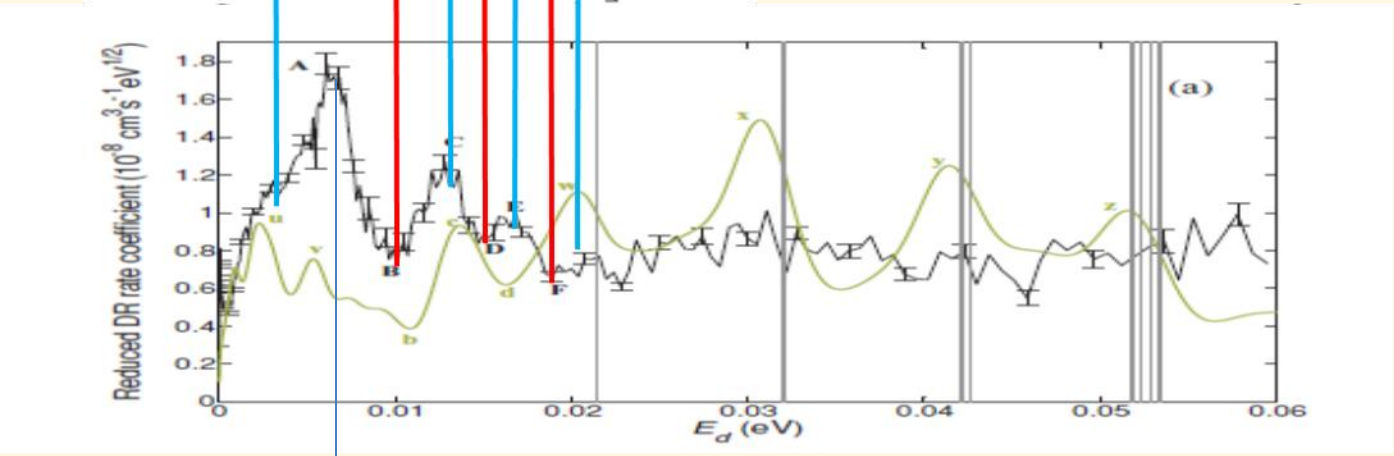


Lifetime graph for
rotational resonances
[blue for paraH_3+ (1,1) to (2,1)]



There seems to be a correlation between the peaks and valleys





Note: The “A” peak has no counterpart.
Maybe it comes from rotational excitation (2,1) to (3,1)

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

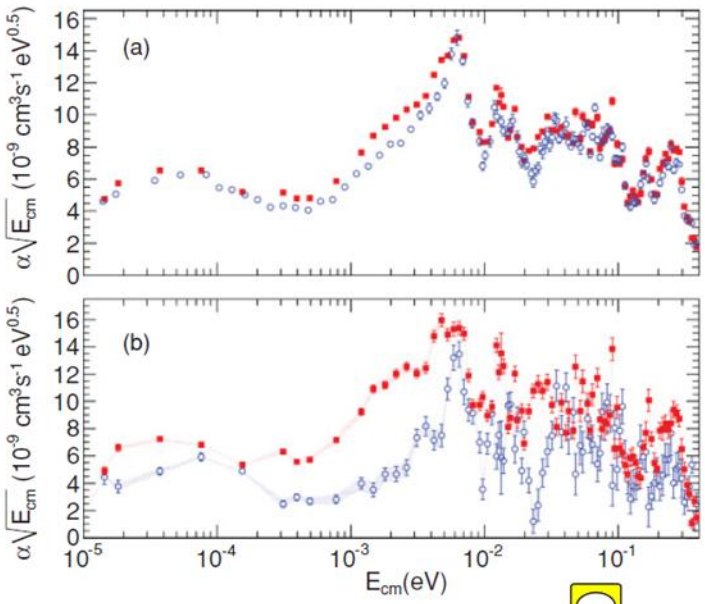
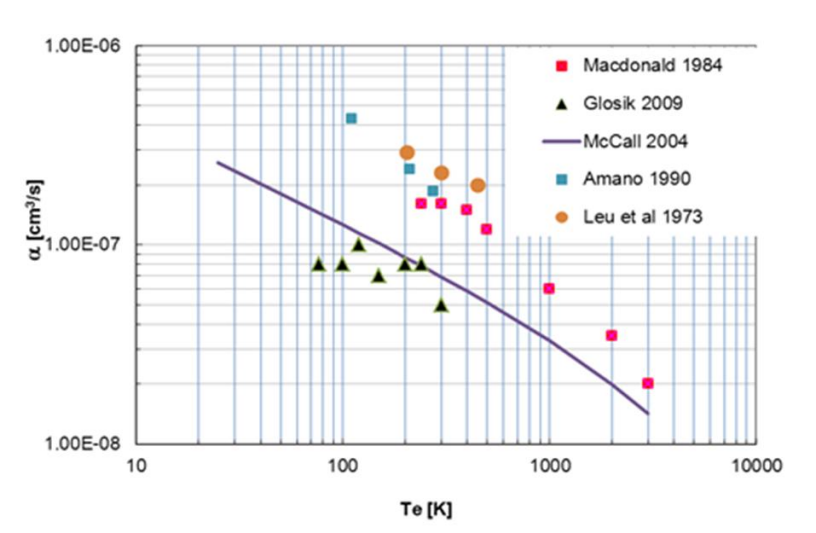


FIG. 8. (Color online) Comparison of the DR rate coefficient for different nuclear spin modifications of H_3^+. The upper panel (a) shows the results obtained with the supersonic expansion source and 1:5 n-H_2:Ar (blue circles) and 1:5 p-H_2:Ar (red squares) mixtures. The lower panel (b) shows the extrapolated 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.

~~Conclusion~~ Speculation

- H_3^+ recombination around 77 K is largely due to para H_3^+
- Two rotational resonances contribute (1,1) to (2,1) and (2,1) to (3,1)
- The storage-ring thermal rate at 77 K may be a bit large (too much para in (2,1)?)



On the other hand:
Something "problematic"* may be happening in the storage rings

*Petrignani et al , PHYSICAL REVIEW A 83, 032711 (2011)

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".