Strong ro-vibrational excitation in high flux expanding plasmas

Influence of volume and surface processes and negative ion production

Daniel C. Schram
Eindhoven University of Technology, The Netherlands
FOM-Institute Plasma Physics, Nieuwgein advisor
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Work from: O. Gabriel, R. Engeln, T. Hansen, R. Zijlmans, J.van Helden, G. Yagci,

Contents:

- **Surface association H_2(r,v)**
- **Surface mechanisms**
- **Importance chemistry: H^+ & H^-**
- **Molecules at surface in N_2, NH_3, O_2, NO**
- **Molecules in H-N-O-C**
- **Global picture?**

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Plasma physics/chemistry- group PMP:
M. van de Sanden,
R.Engeln, E.Kessels, A.Creatore,
R. Pipino, E.Aldea, O.Gabriel, G. Ledru
G. Yagci, R. Westerman, I. Martin,
S.Starostine, P.v.d.Oever,
PhD: J.v. Helden, R.Zijlmans, J.Gielis
S.Heil, B.Hoex, I.Volintiru, T. Hansen
E.Langereis, M.Petcu, P.Gevers,
H.Knoops, K.Nadir

A.Husken, M.v.d.Sande,H.d.Jong
J.Jansen, J. Zeebrechts;
Secr. J.Loonen, L. Doms

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J. Röpcke, G. Lombardini, O. Gabriel, S. Welzel, S. Stancu

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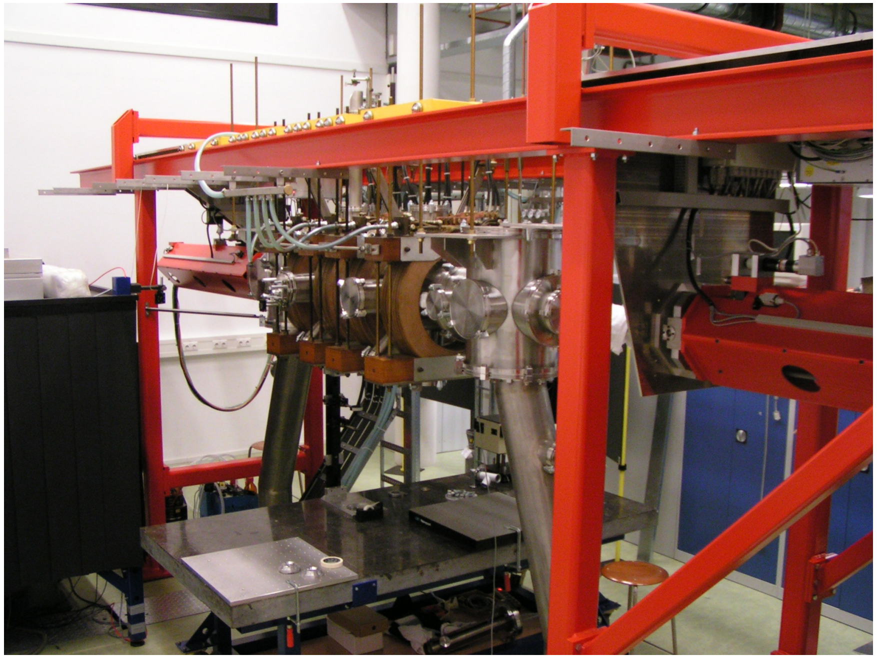
labs



H_2(r,v), H plasmas

Deposition (a-C:H)

$H + H \rightarrow H_2(r,v)$

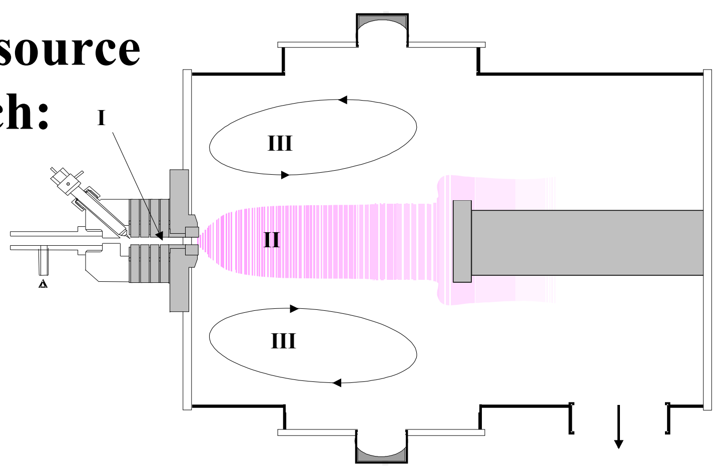
- **generation of (excited!) molecules $H_2(r,v)$ at high flux H atoms**

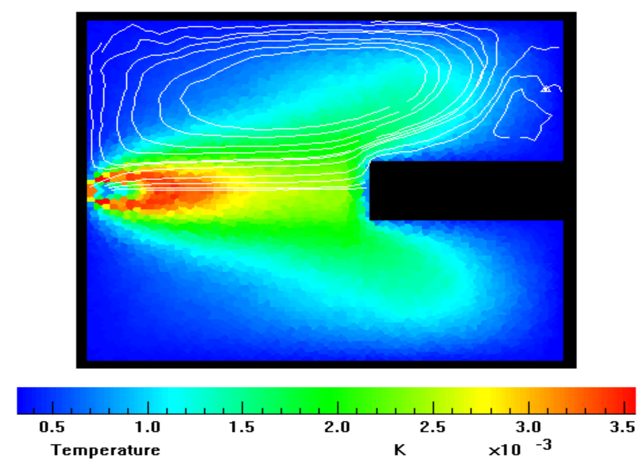
- **Accidentally found in search for fast deposition processes:**
  - ***Anomalous recombination* of atomic ions (MAR)**
  - **High *rotational(and vibration)* excitation**

Fast deposition: m^2 and nm/s: large fluxes of radicals: $10^{22} – 10^{24}$ m^{-2} s^{-1}
high flux to surface: 10^4 ML/s: other situation?
High flux of precursors: high gas & energy efficiencies, like particle sources

Plasmas: ionizing → recombining; plasma dissociates, surface associates

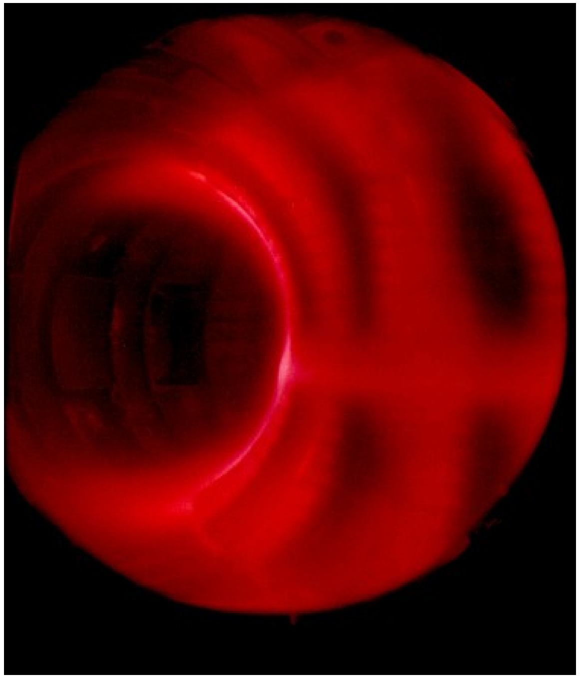
Remote source approach:





Fusion/ astrophysics

Nuclear Fusion: JET



Astrophysics

IC 1396 H-Alpha Close-Up ,Nick Wright, University College London

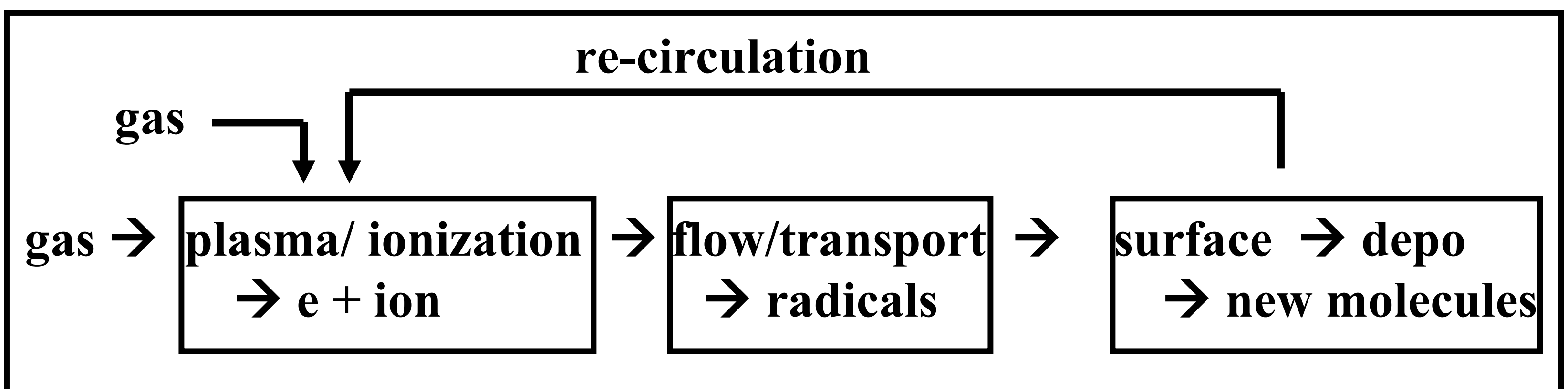
H_α light: could be from molecules + ions

Summary approach

Is plasma different from CVD/ Catalysis?:

Radicals (%) dominate surface → passivated surface

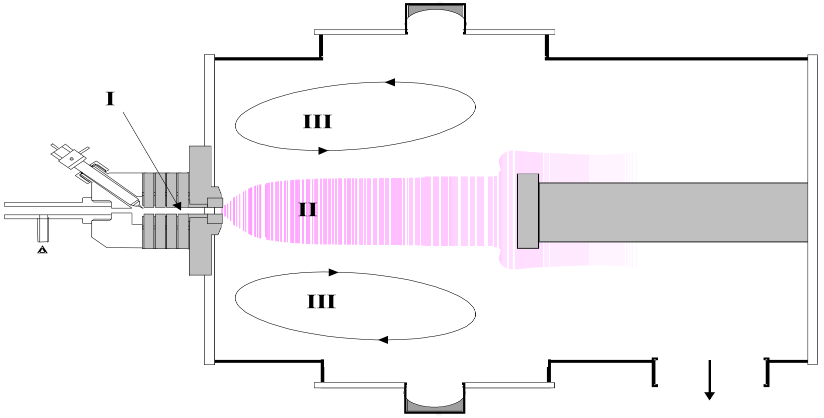
1. **production plasma**
2. **production radicals**
3. **transport: radicals may be transformed , but remain radical**
4. **radicals to surface, reflect, built up density, finally absorbed**
5. **adsorbed fragments give new molecules, which desorb**
6. **new molecules add to injected molecules: gas may change totally!**



Fast depo a-C:H with ETP method

- 10 % ionized plasma beam: Ar^+, expands: high n_e, low T_e=T_h plasma
- Charge transfer & dissociative recombination produce C_2H radicals (and H)
  - $Ar^+ + C_2H_2 \rightarrow C_2H_2^+ + Ar$
  - $C_2H_2^+ + e \rightarrow C_2H + H$; → → surface depo + H_2 generation
  - *Radical production & recombination* of atomic ions from source

With expanding thermal plasma (ETP) method: Remote source deposition
High flux of precursors: high deposition rate + generation (H_2..) molecule



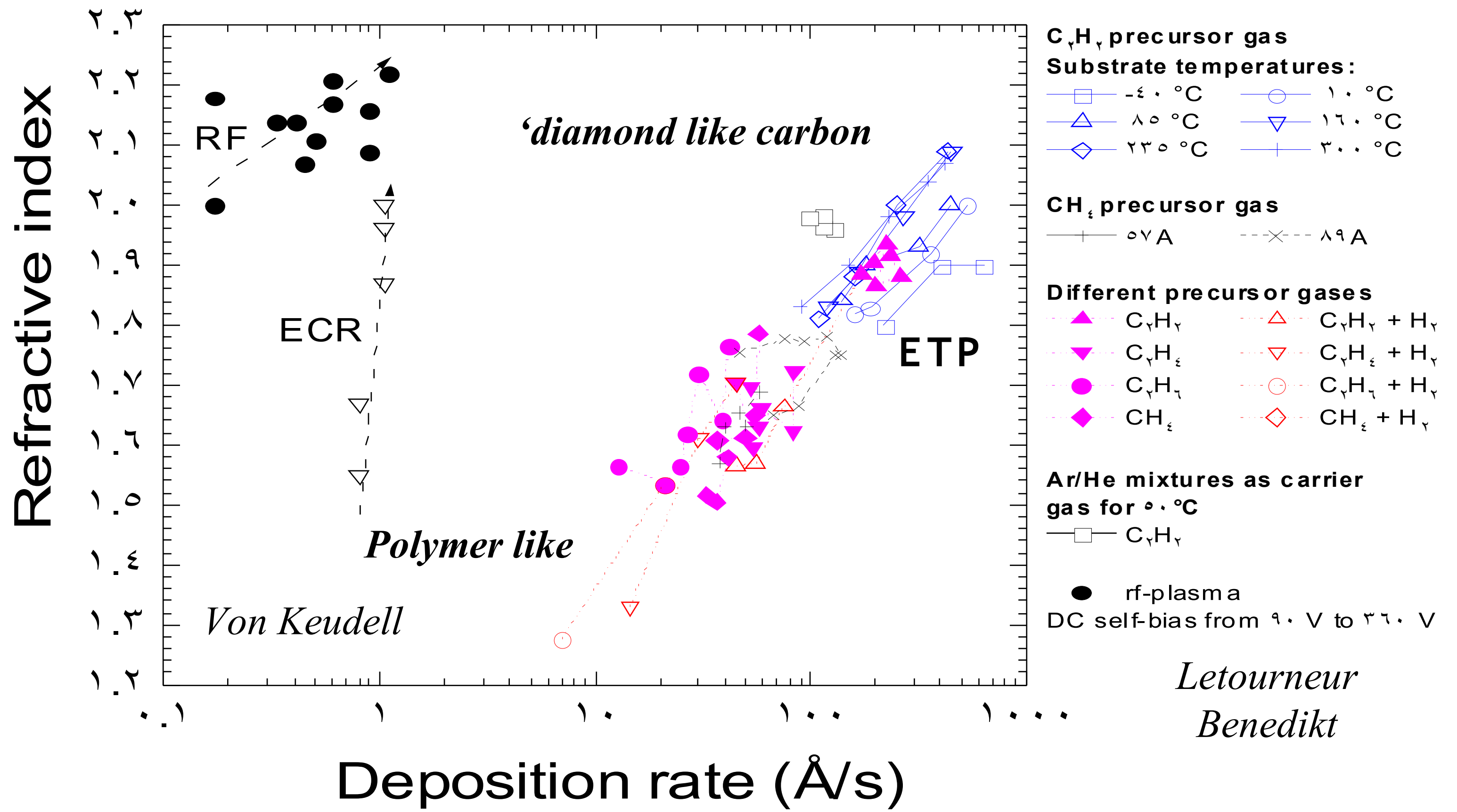
Note: wth CH_4: C_2H_2 & H_2 production & depo

Results fast deposition, a-C:H, ..

Fast deposition 100 nm/s of diamond like carbon: DLC

example: higher growth rate: better, more dense, hard thin layer!

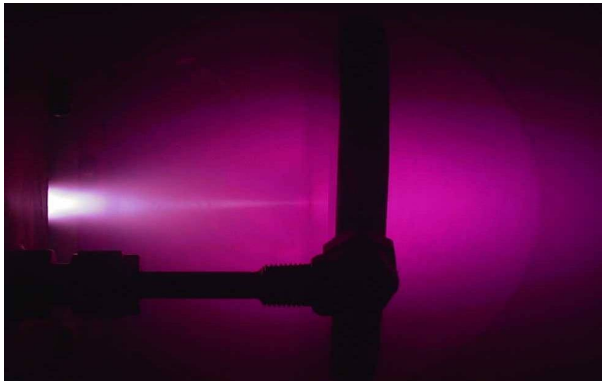
Q: deposition *“physical” or ”chemical”?* ”Ion pinning” *and* ”radical radical”?



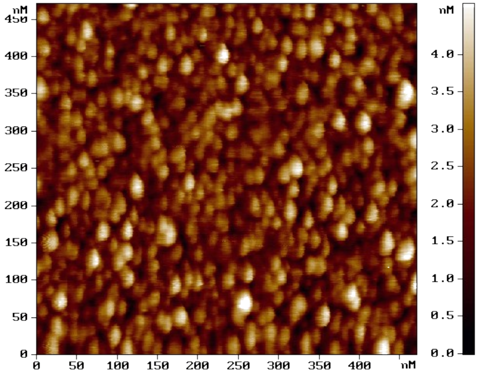
Quality depends on $T_{substrate}$ & rate , ***not on injected mol: CH_4, C_2H_4, C_2H_6.. C_2H_2***

Use of H atoms: fast deposition a-, nc- Si:H

- Also H atoms can be used for radical production:
  - Ar/H_2 in source → mainly H atoms
  - H atom source: H + SiH_4 → SiH_3 +H_2; SiH_3 soft radical: depo good a-Si:H
  - High rate 10 nm/s at elevated $T_{substrate}$ 400 C



nc-Si:H



With more H atoms: nano crystalline layers: nc Ci:H

more SiH_2, SiH, Si = harder radicals?

Type radical determines structure/ quality layer. Is it the only solution?

Can we separate deposition + annealing? achieve higher rates! : mechanism: strategy

Deposition: Motivation for H ←→ H_2(r,v) high flux

Questions:

In how far is mechanism essential for reaching dense material and proper structure.

Is amount of H atoms essential ingredient?

Is it the essential factor for nc-Si:H?

Is r,v excited H_2 an important factor?

Other questions:

Is depo + annealing an (fast) alternative?

Is the exact nature of radicals important? Or is it more chemical?

→Mechanism of deposition at surface and mechanism of molecule formation at high flux

Cool expanding plasmas (T ~ .3 eV)

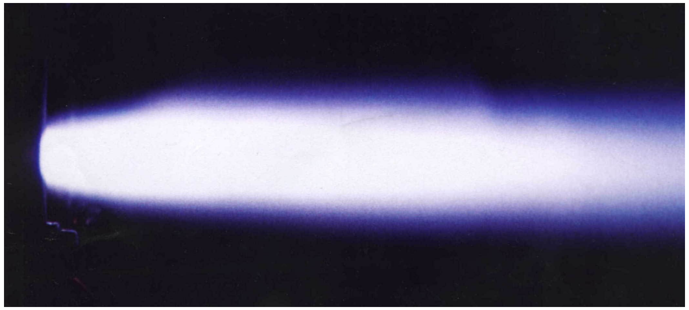
In remote source approach: ETP!

high flux radicals and/or ions

simple heavy particle kinetics: charge transfer/ abstraction..

low T_e: no e- excitation/dissociation

Light: signature of ions/electrons + molecules



Ar, Ar^+ e expansion:

weak (3p) ion recombination

→ *4p-4s red emission* + *blue continuum*

With H_2: Ar/ H_2 expansion:

strong recombination by:

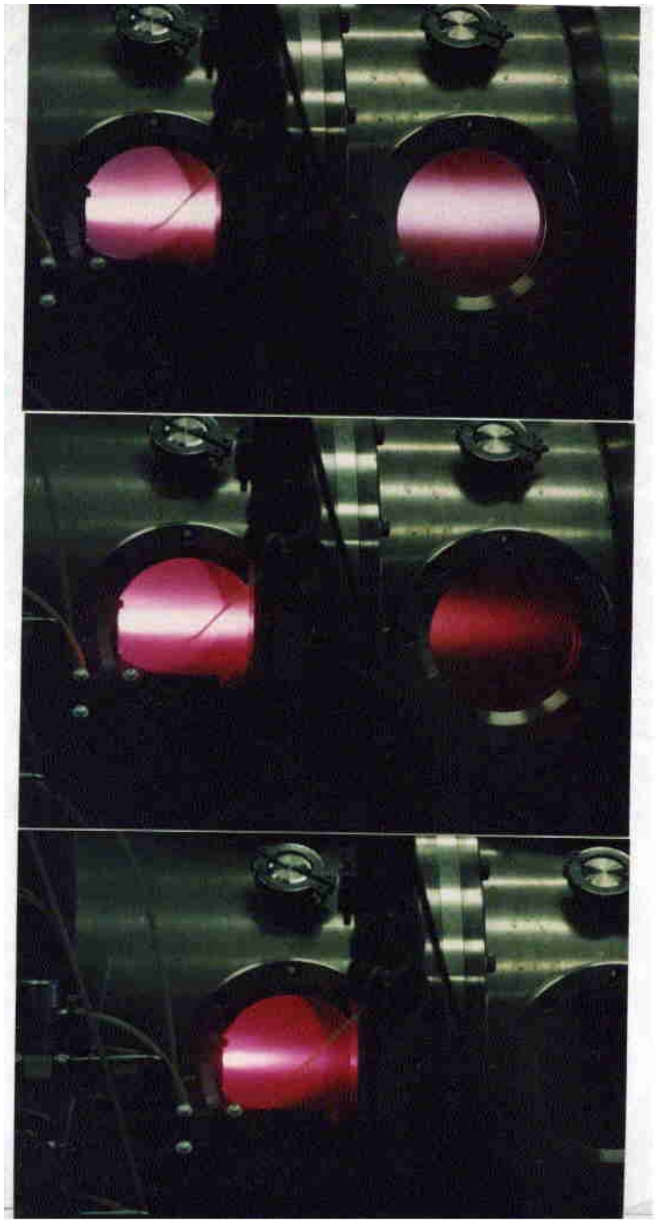
$Ar^+ + H_2 \rightarrow ArH^+ + H$,

$ArH^+ + H \rightarrow H + H^* \rightarrow$ *Balmer α*

Pure H_2 expansion: even stronger recombination:

"MAR" molecular assisted recombination

Effect of H_2 molecules



Ar plasma
+
< 0.1% H_2

1% H_2

5% H_2

Effect of H_2 molecules on Ar plasma expansion: MAR!

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

$$ArH^+ + e \rightarrow Ar + H^*$$

Balmer α

40 Pa: $n_{H2} \sim 10^{19}\ m^{-3}$

Kinetics with molecules: H_2, …

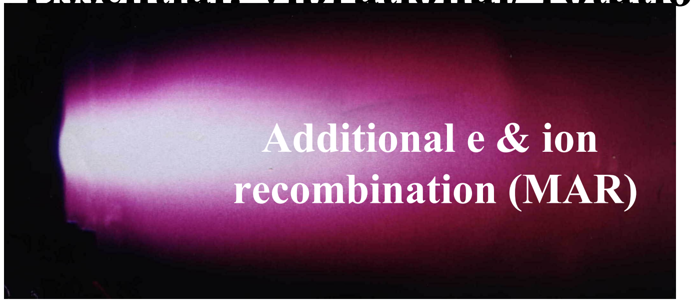
Pure H_2 expansion: very strong recombination at lower n_e: MAR

$H^+ + H_2(r,v) \rightarrow H_2^+ + H$; $H_2^+ + e \rightarrow H + H^*$, red light

$e + H_2(r,v) \rightarrow H^- + H$; $H^- + H^+ \rightarrow H^{***} + H$, blue light

At high electron density ($n_e > 10^{19}$-10^{20} m^{-3}): H*--H* re-ionized.**
But at lower densities: catastrophic decrease of ionization:
very fast loss of ions and electrons and thus light

Essential: vibrational/ rotational $H_2(r,v)$



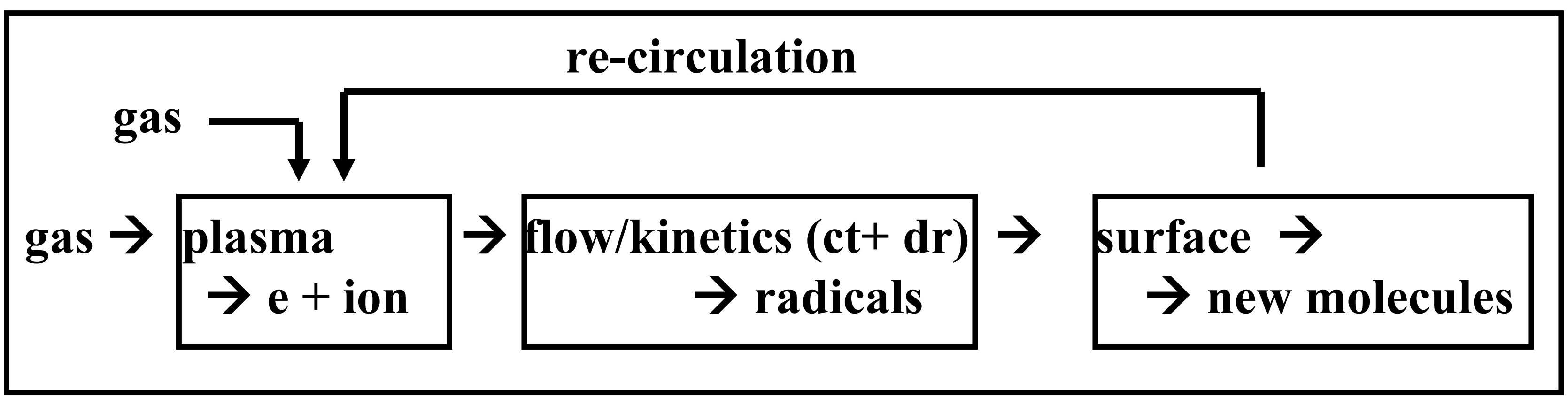
Similar (but less fast): with other molecules: O_2, N_2, CH_4,…

Summary kinetics

Plasma dissociates (by MAR..), surface associates:

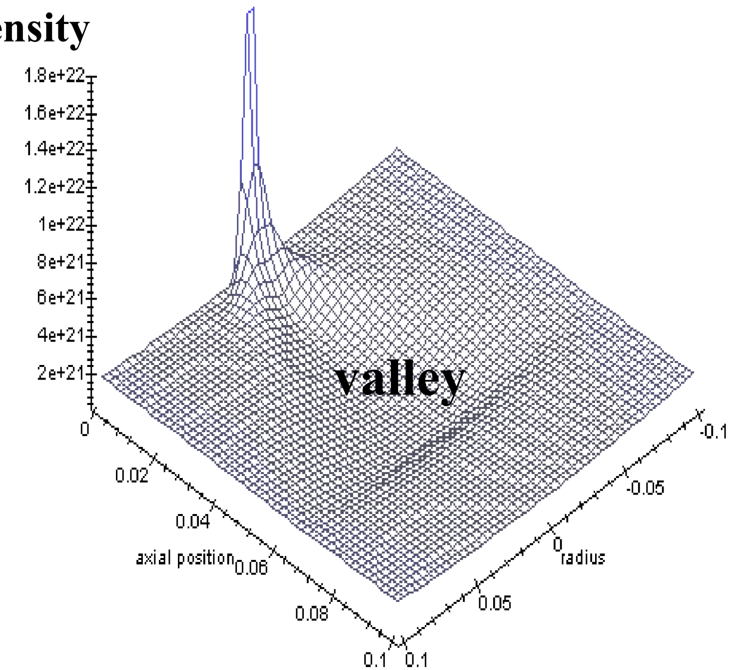
1. Plasma: ions + electrons: + molecules:
2. Charge transfer + dissociative recombination → radicals
3. Radicals remain radicals during (fast) transport to surface
4. Radicals to surface, reflect, built up density, finally absorbed
5. Adsorbed fragments give new molecules, which desorb
6. New molecules add to injected molecules: gas may change totally!

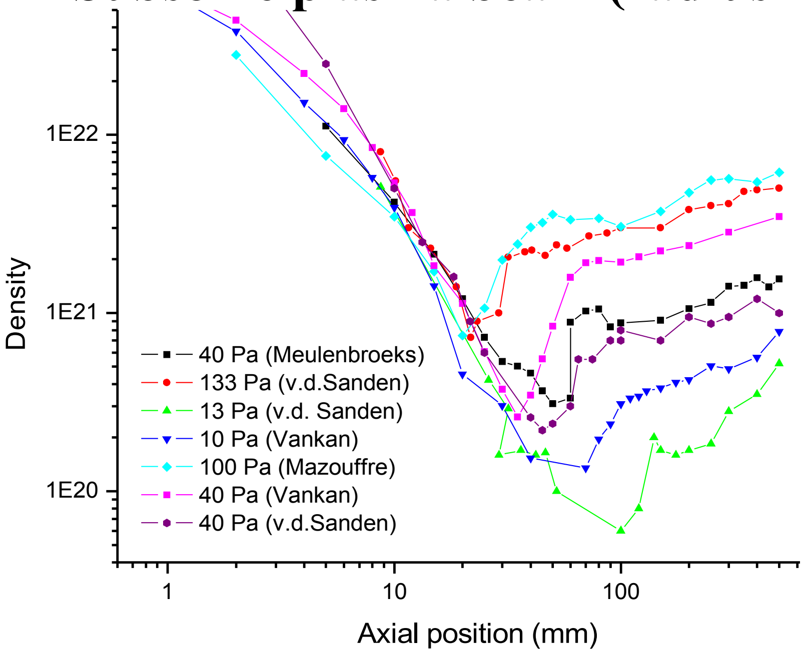
Note: desorbed molecules are not so dependent on type radical



Expansion, plasma beam, recirculation

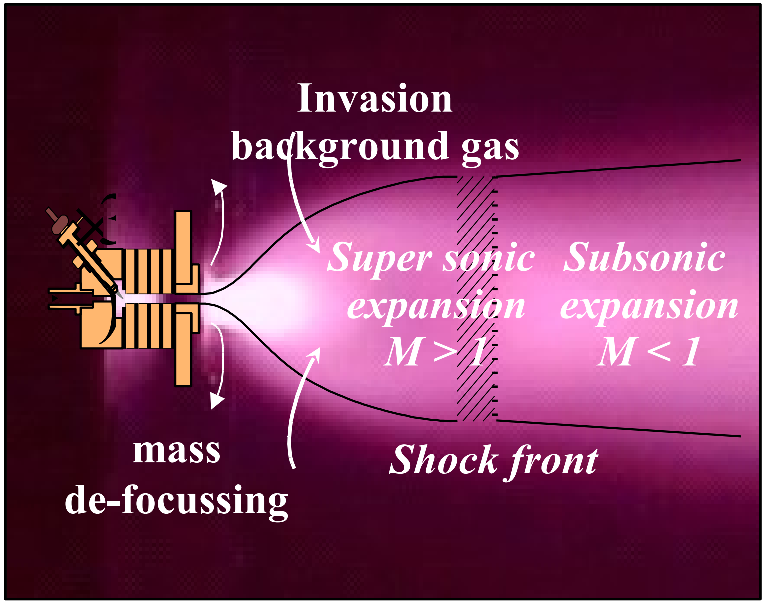
Expansion: supersonic
density ~ z_0^2/z^2; (z_0 ~ radius source)
temperature adiabatic $T/T_0 \sim (n/n_0)^{\gamma-1}$
velocity: at exit sonic, $c_0 \rightarrow 2c_0$
"Valley" just before shock front
Stationary shock front:
$z_M = 2\ 10^{-2}\ (flow/p)^{1/2}\ (AT_0)^{1/4}$, flow in scc/s
Subsonic plasma beam (radius ~ z_M):

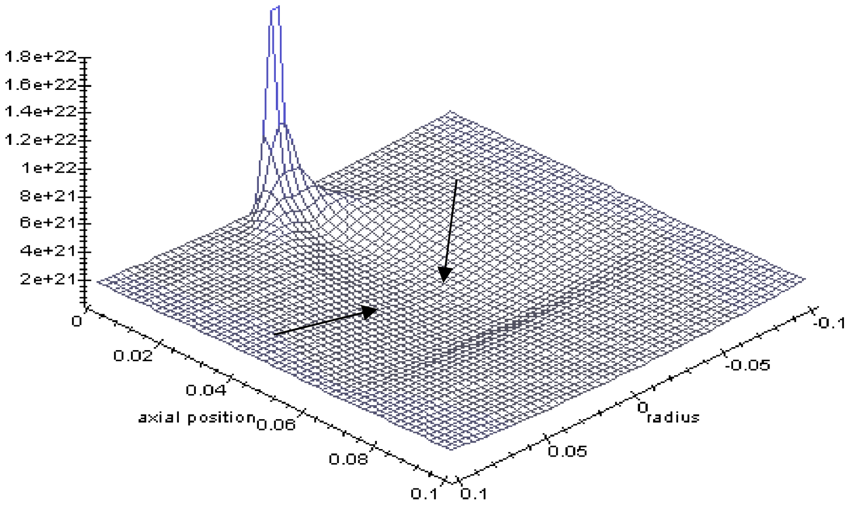




plasma expansion + beam: .3 msec
Re-circulation: 10 msec
Residence time: 1 sec

Invasion & mixing in from background





Mass de-focusing: light particles scatter out

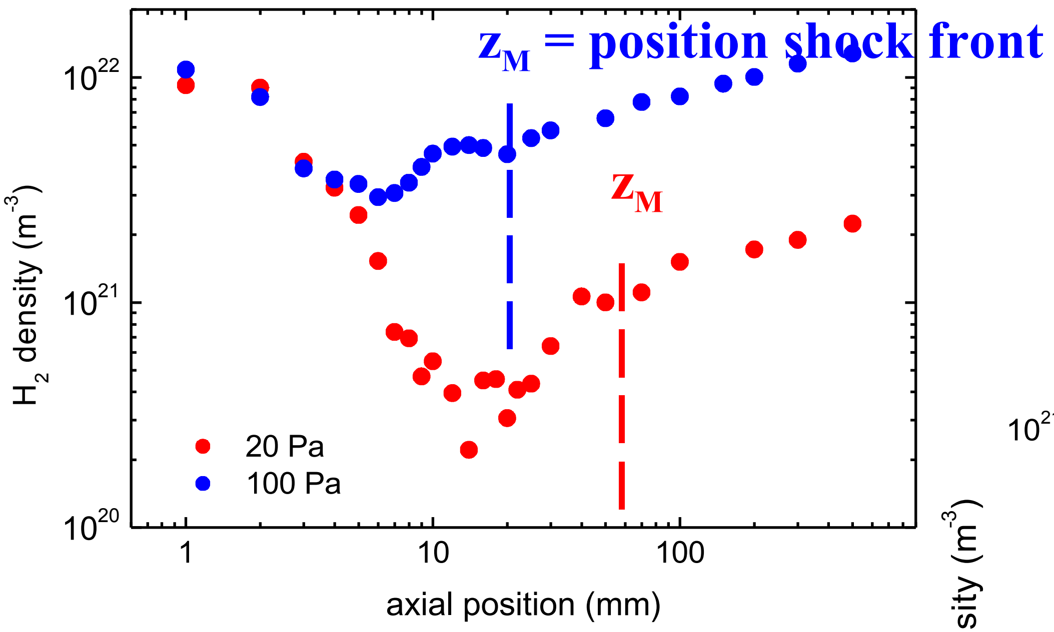
Invasion: rarefied conditions: $\lambda_{mfp} \sim z_M$ good mixing in supersonic part

Here favorable for chemistry: supersonic velocity/ high T_{heavy}

Also in forward plasma beam: T ~.3 eV , high r,v excitation?

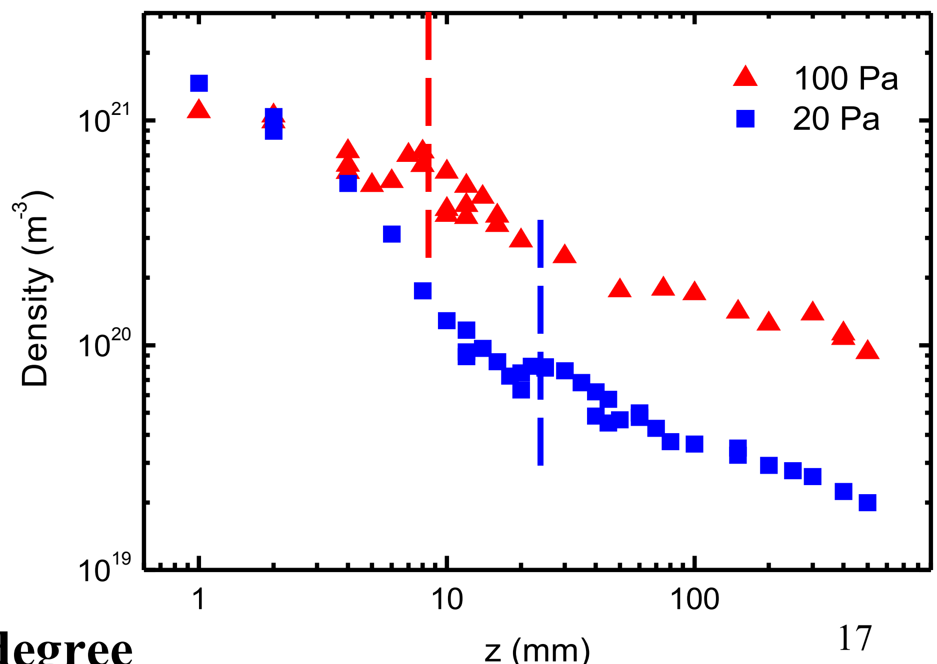
Expansion: z dependence: $1/z^2$ density

$n(H_2)$ Rayleigh scattering



H_2 density follows $1/z^2$ law

n(H) Two photon LIF (TALIF)



H density weaker z-dependence
→ reflected H atoms?

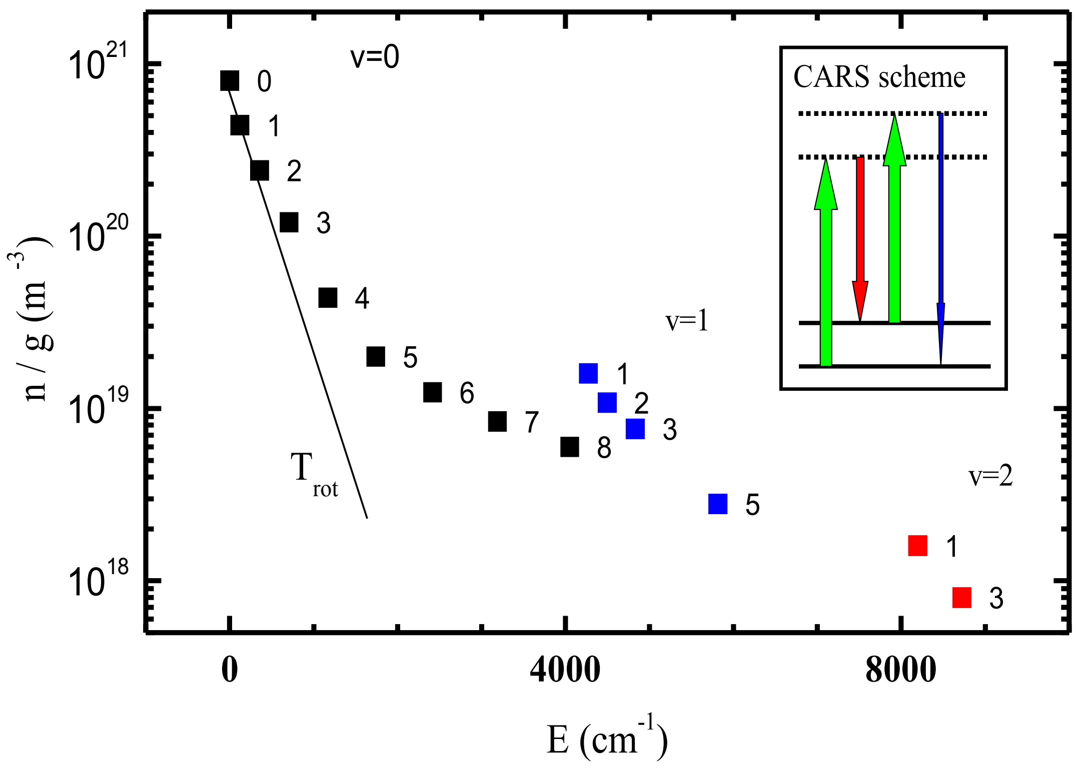
→ apparent increasing dissociation degree

Molecule generation

Presence $H_2(r,v)$: CARS

$H_2(r,v)$ First measured by CARS: Coherent Anti-Stokes Raman Scattering

Meulenbroeks et al PRL



At z = 8 mm from source

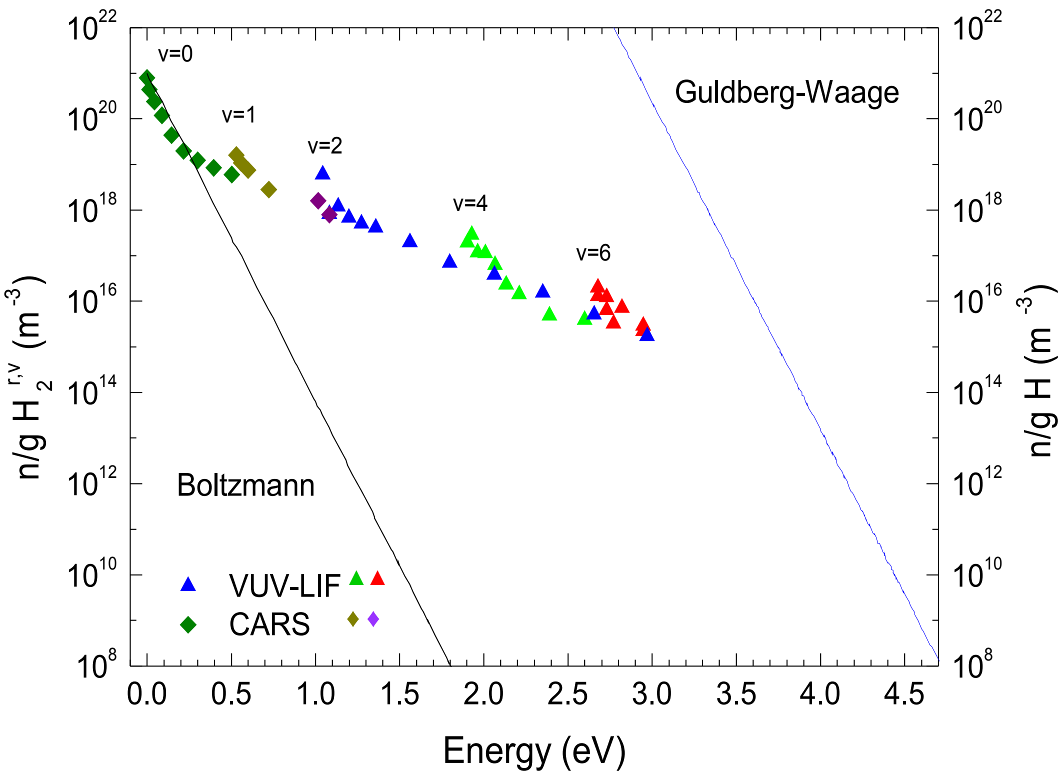
H_2 plasma, Φ_{H2} = 3 slm

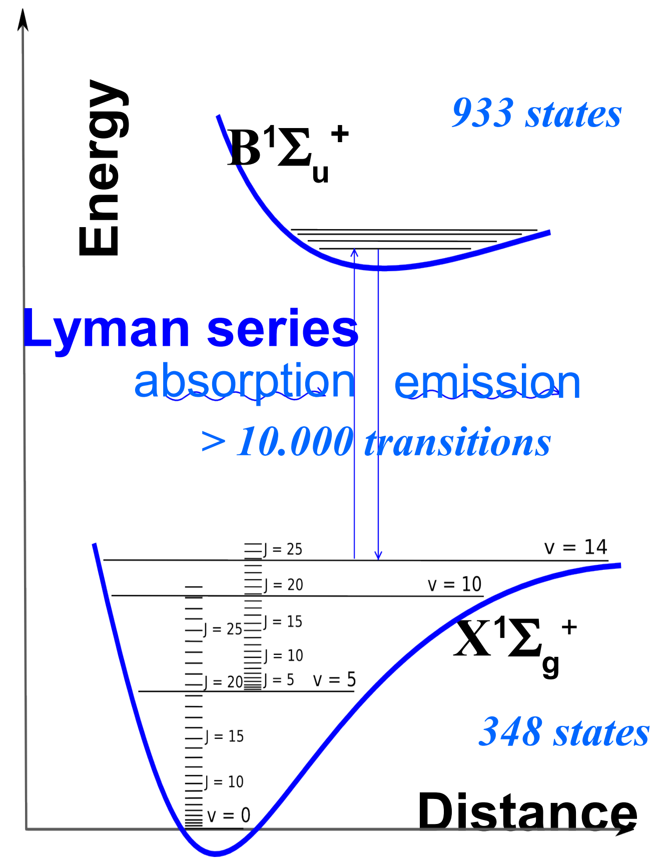
p = 50 Pa???

Total pressure from measurements: Σ n(v,J), T_{rot} → p_{vessel}

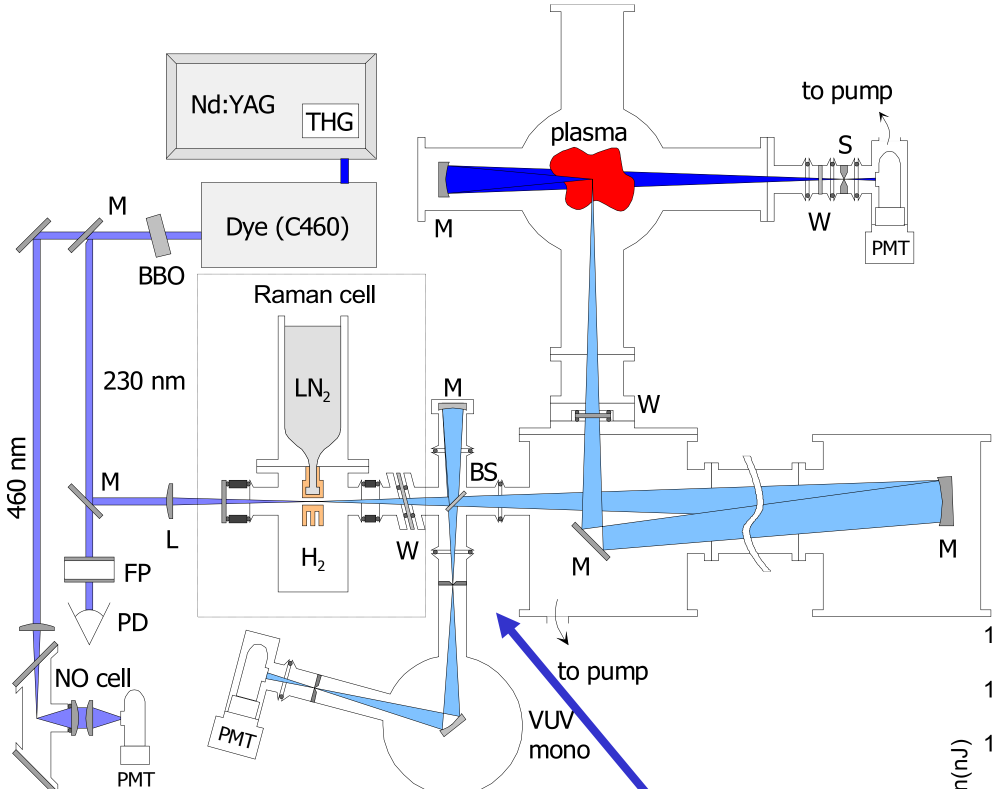
$H_2(r,v)$ with VUV-LIF

Vacuum Ultra Violet Laser induced fluorescence
Excited with several anti-Stokes lines (Vankan, Gabriel, Engeln et al)

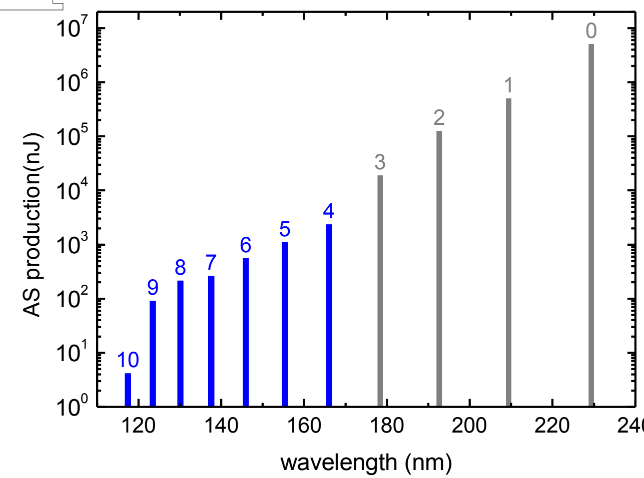




Methodology: Multiplexed VUV-LIF



VUV photons by Raman generator: SARS



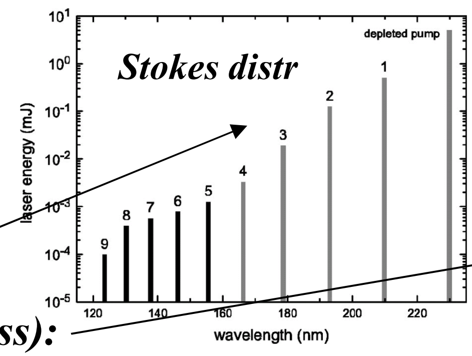
Multiplex-VUV-LIF => Simultaneous excitation → more v,J-information:
also surprises: high J population!!

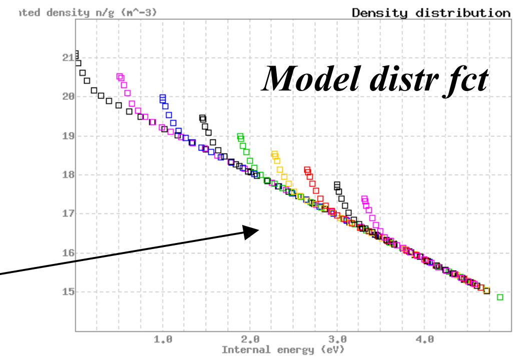
Multiplexed-VUV-LIF

Input:

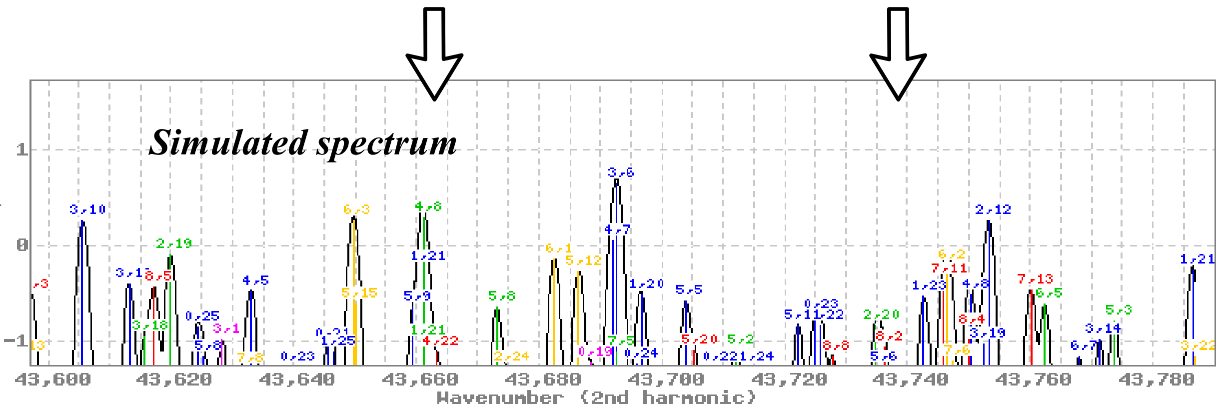
- *Spectral data (Einstein coefficients, life times),*
- *Transmission of optical components,*
- *Detector efficiency,*
- ***Laser power (Anti-Stokes distribution),***
- ***Model for the H_2 density distribution (first guess):***

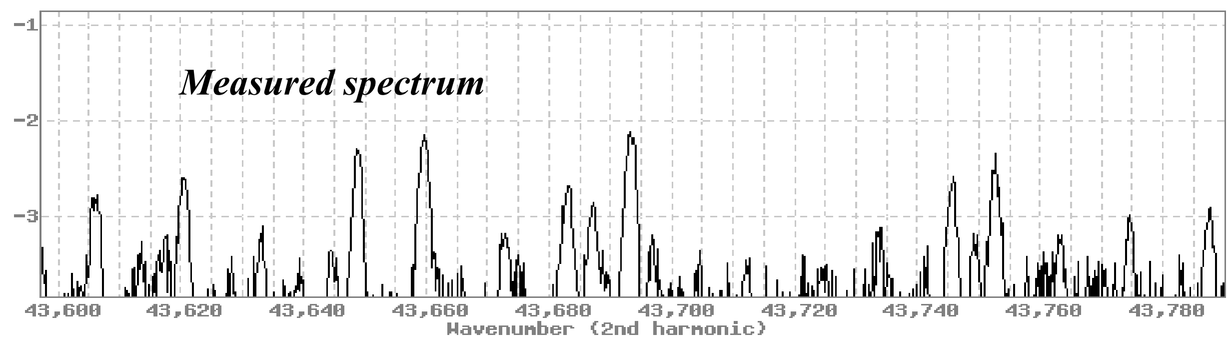
Multiple hockey stick



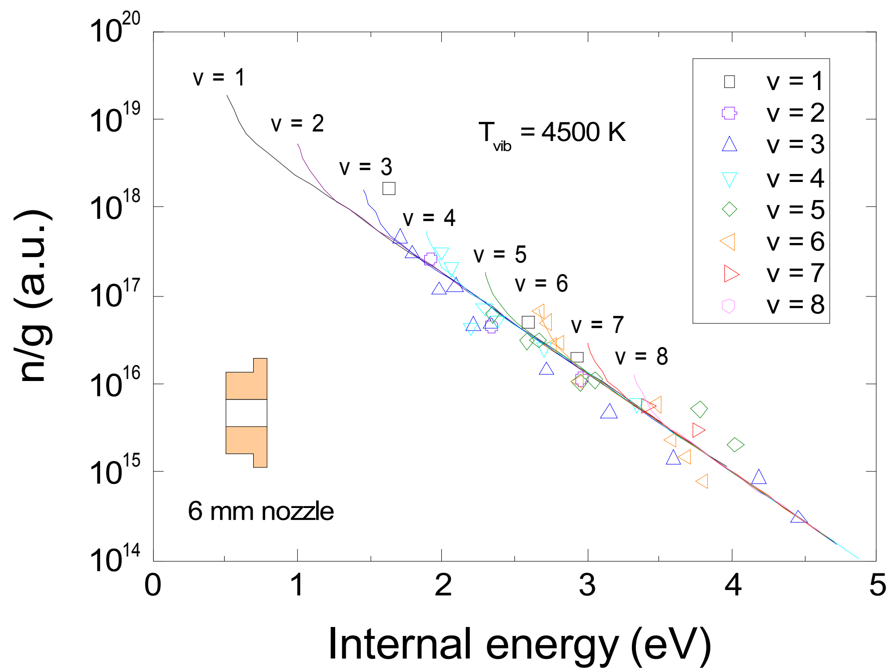


→Multiple hockey stick distribution

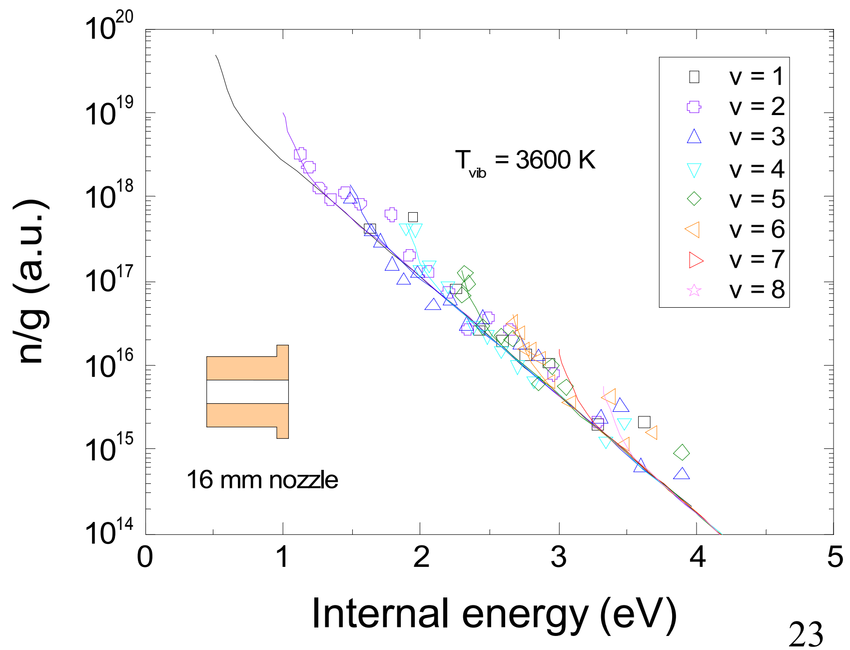




New results $H_2(r,v)$

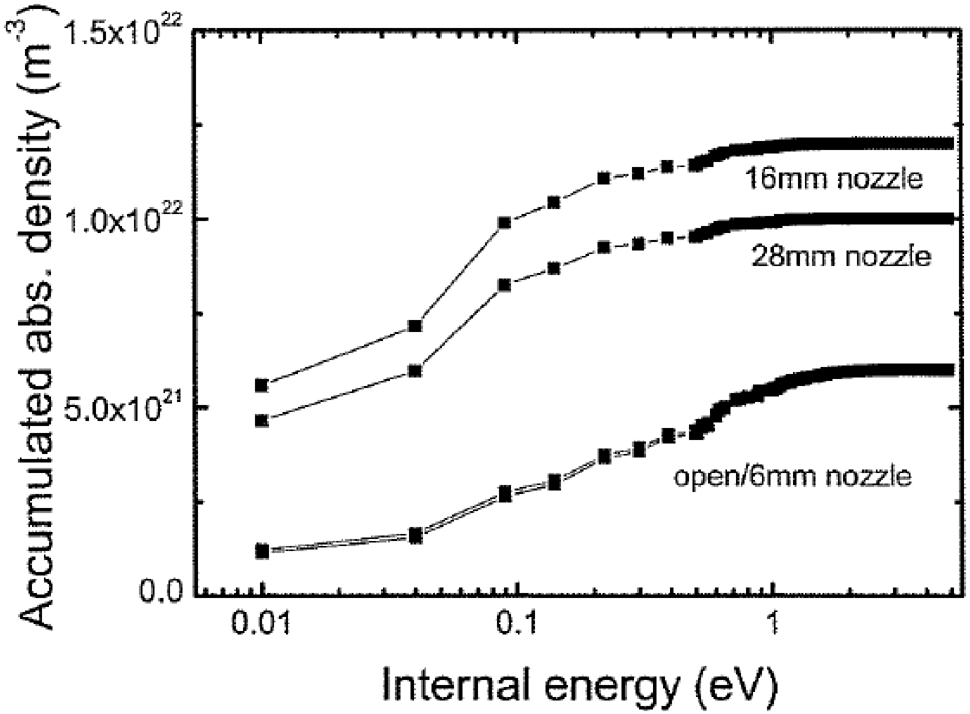


Short nozzle:
Population up to close to continuum:
higher source T, higher H-flux

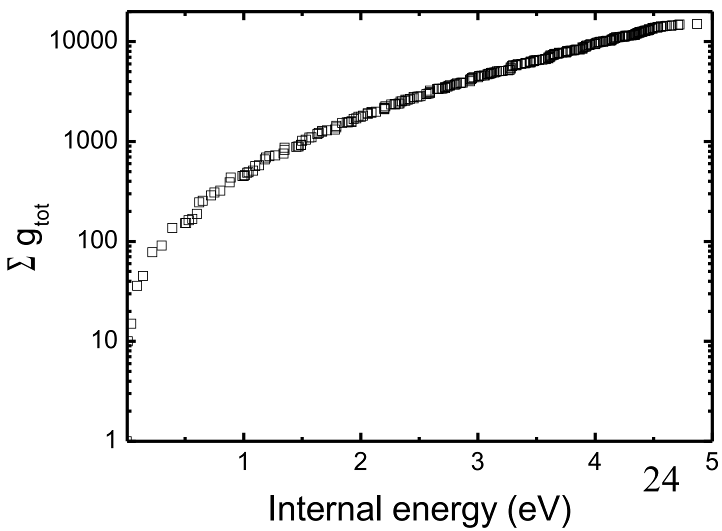


Long nozzle:
Population smaller (still to continuum):
lower source T_s,
H already lost – $H_2(r,v)$

Importance density H_2(r,v: accumulated statistical weight G



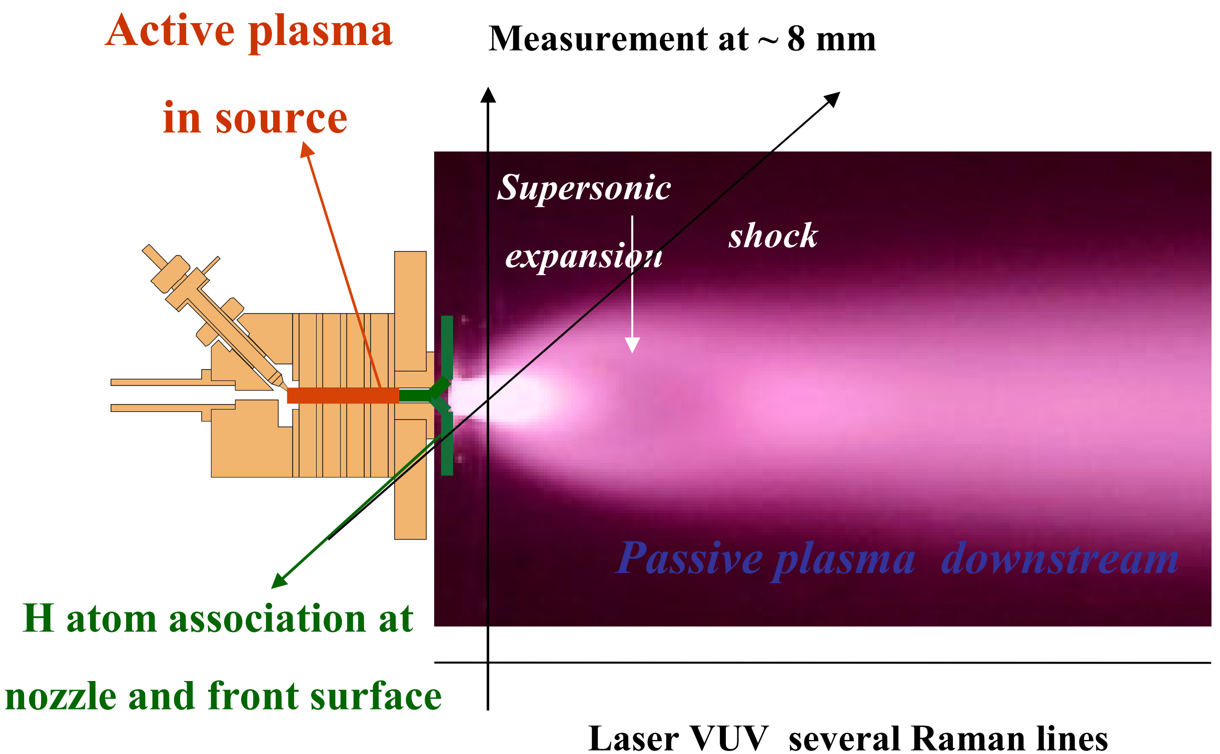
Accumulated density $\Sigma H_2(r_i,v_j)$



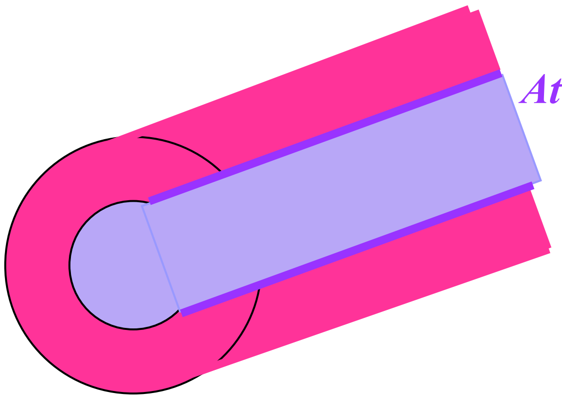
Importance rotational excitation:

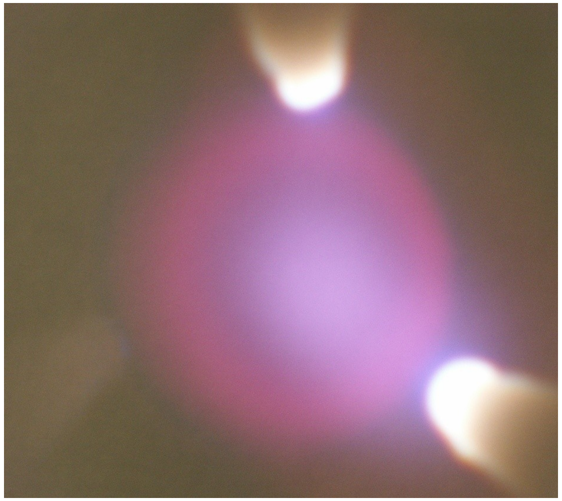
- **Larger rates for e + H_2(r,v) → H^- + H**
- **Large statistical weight: rotation: 2J + 1**
- **sizeable density!**

Molecules produced at surface exit nozzle arc.



In arc: atomic with small



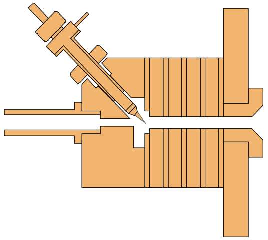


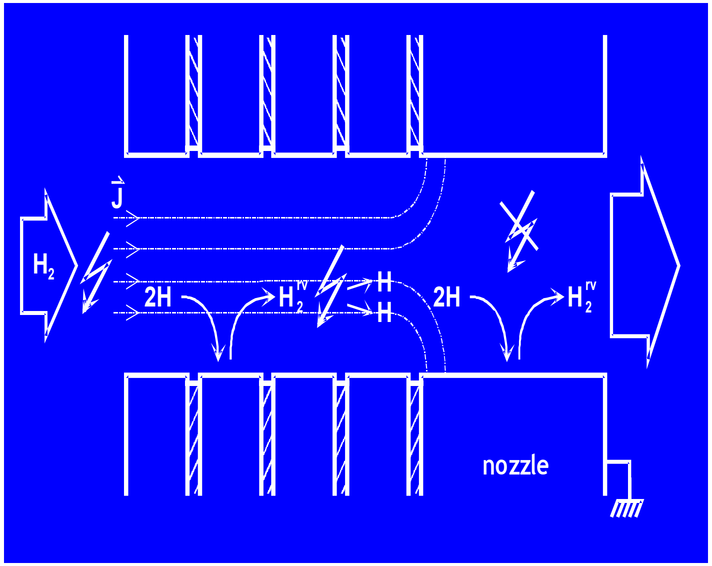
Atomic centre plasma H atoms, H^+ions/ electrons (10%):
Light: mainly continuum (and H_n lines)

"Molecular" periphery: still mainly atoms, some molecules, no ions/ electrons

At interface: out-diffusing H+ ions (charge transfer with H_2)→ H_2^+
H_2^+ + e → H* + H, as ne is too low then H* → H^+ photons (H_α, Ly_β)
Number of molecules needed to kill at interface

Processes in arc



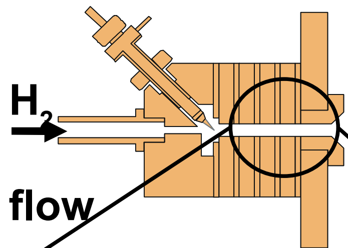


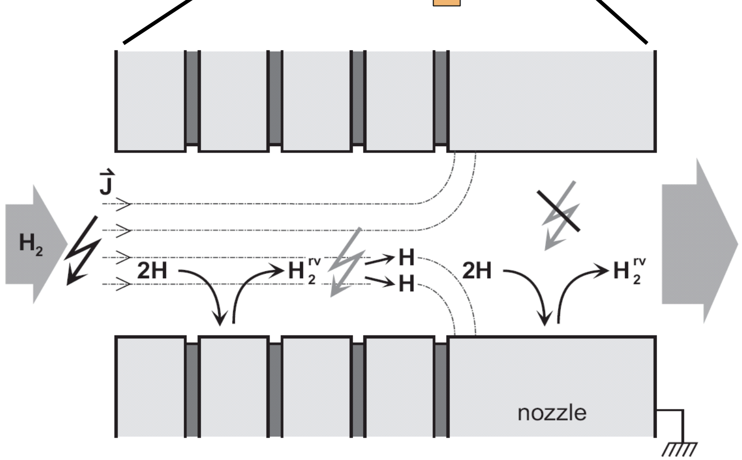
In arc: atomic centre: H, H^+, e
In periphery: mainly H to surface, some H_2
$H_2(r,v)$ from surface, diffuses inward
Kills electrons/ions at interface

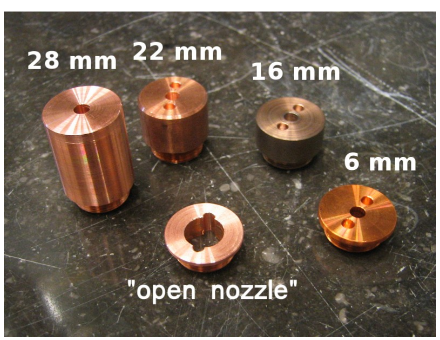
At interface: in atomic centre: H^+, e diffuse outward
in periphery: some H_2 diffuses inward

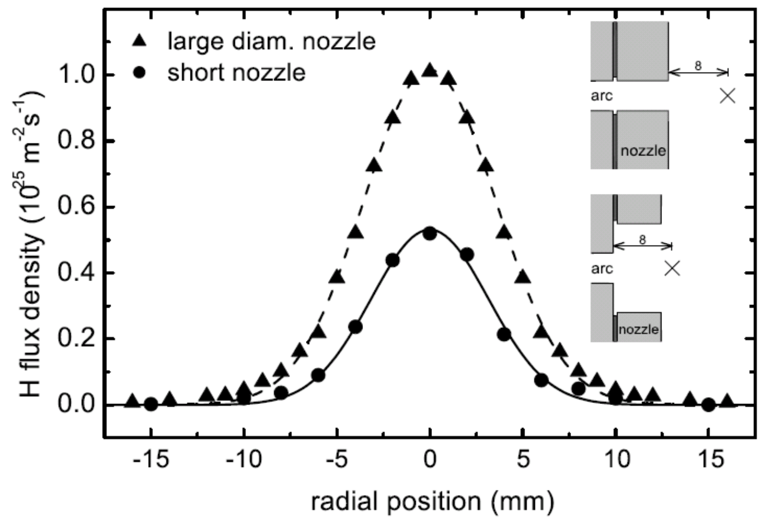
Within interface: $H^+ + H_2 \rightarrow H_2^+ + H$; $H_2^+ + e \rightarrow H + H^*$;
and if n_e is high enough: $H^* + e \rightarrow H^+ + 2e$
Outside interface: n_e is too low and $H^* \rightarrow H$ + photons (H_α, Ly_β)

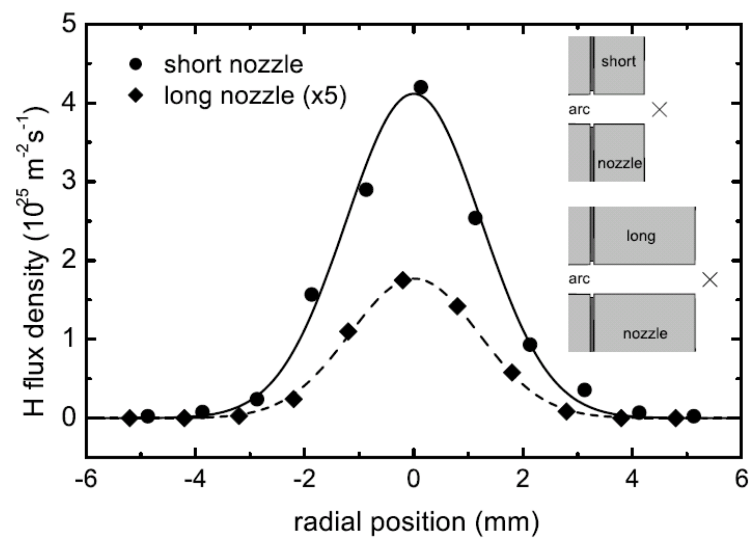
H_2 surface association on nozzle surface variation Nozzle length











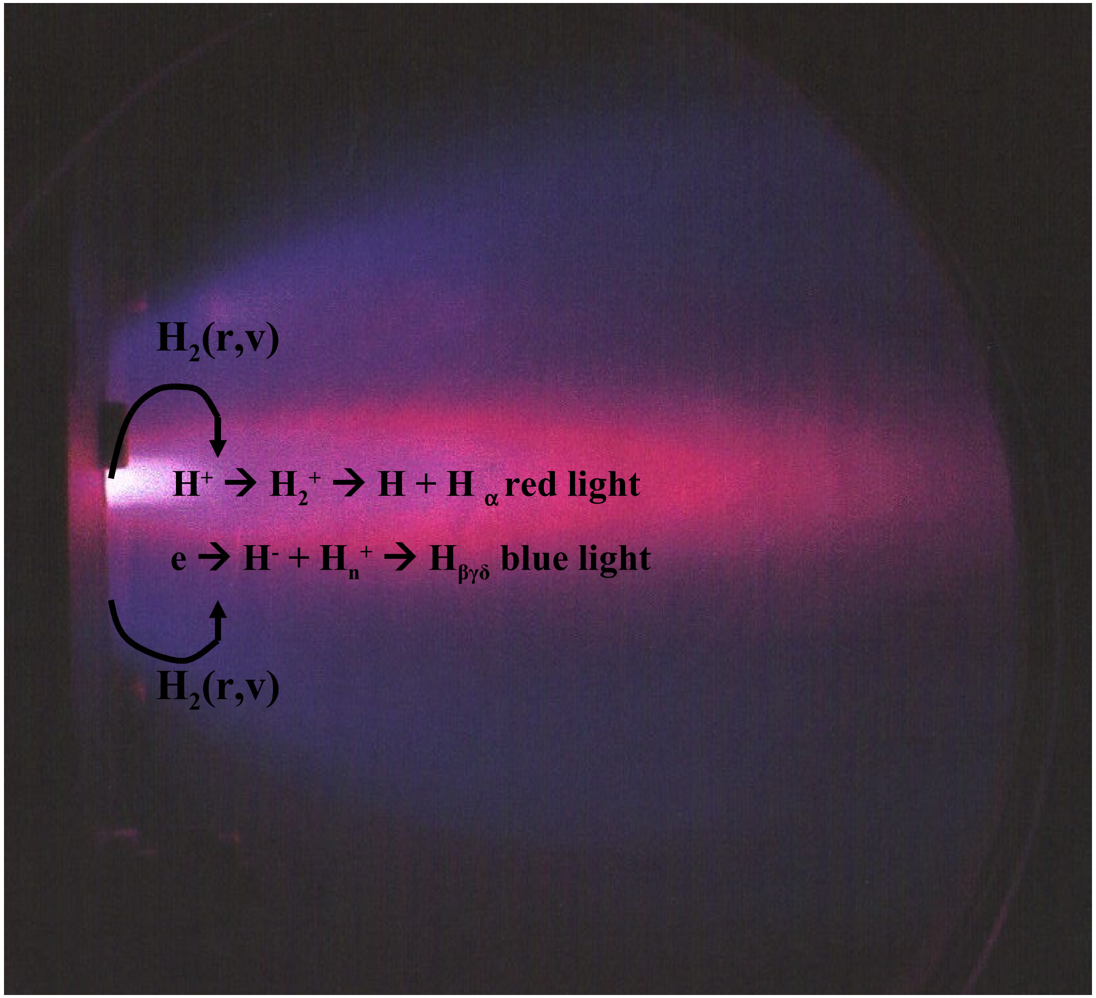
P. Vankan, R. Engeln, D. C. Schram, Appl. Phys Lett. 86, 101501 (2005)

Generation mechanism $H_2(r,v)$

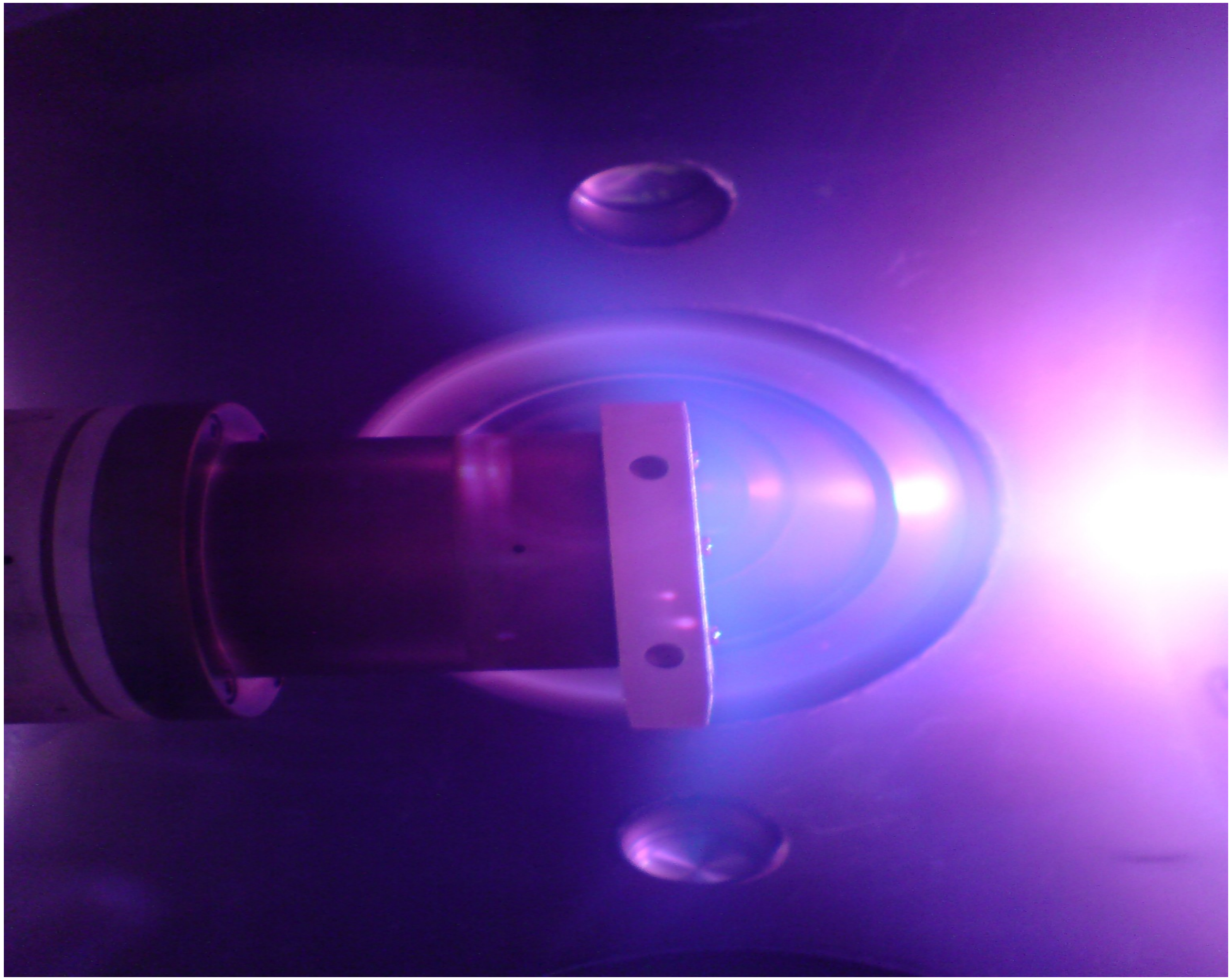
Generation at nozzle surface
High excitation v,J
Incident flux H atoms: >10^{25} m^{-2} s^{-1}

γ? At these hughe fluxes

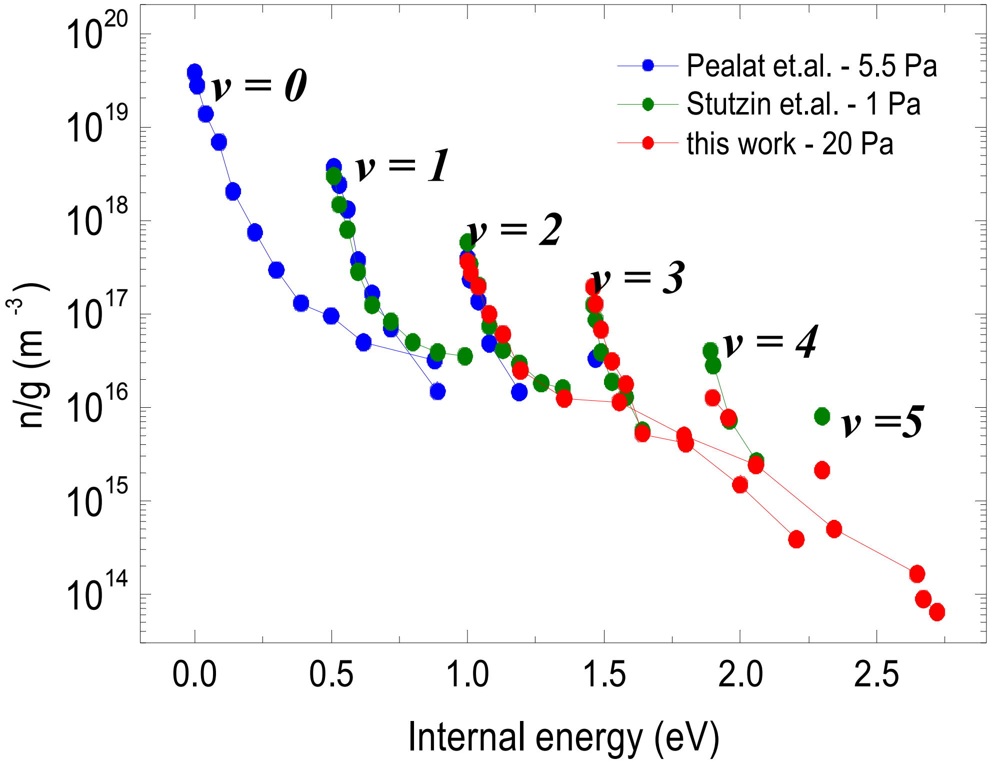
Generation $H_2(r,v)$ in expansion?



Generation $H_2(r,v)$ in expansion near surface?



Excited $H_2(r,v)$ molecules from surface? Other experiments



Experiments in

- **Magnetic multipole**
- **Expanding plasma**

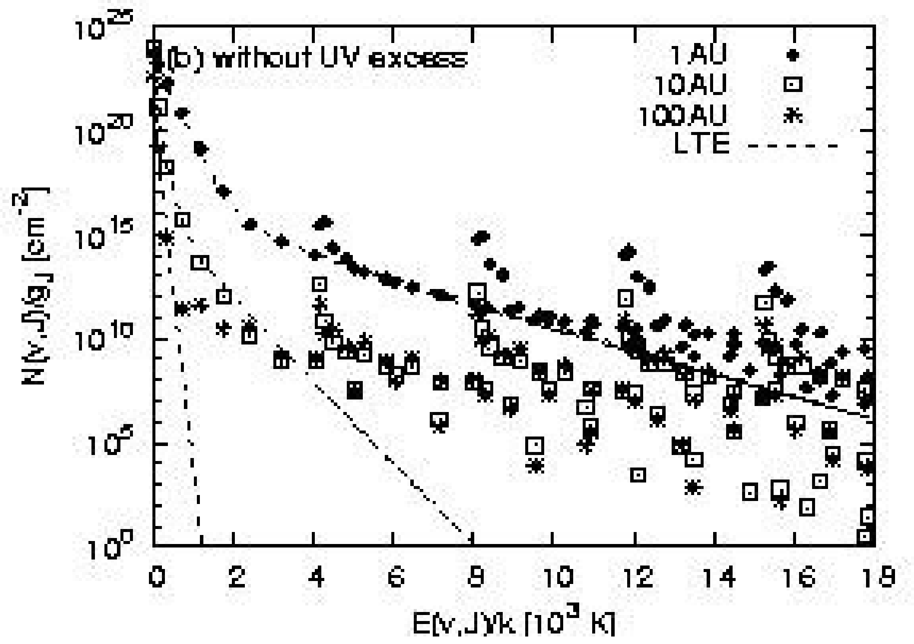
- **Very similar results. Why?**

High J (low v) are unavoidable??

[1] M. Péalat, J.E. Taran, *J. Chem. Phys.* 82, 4943 (1985)
[2] G. Stutzin, A. Young, A. Schlachter, K. Leung, W. Kunkel, *Chem. Phys. Lett.* 155, 475 (1989)
[3] P. Vankan, D.C. Schram, R. Engeln, *Plasma Sources Sci. Technol.* 14, 744 (2005)

Excited H_2(r,v) molecules in space

Calculations T. Millar very similar distributions



Also experimental emission (see yesterdays talk C. Joblin for v=0,1)

High J (low v) are unavoidable??

H.Nomura, T.J.Millar, A&A 438 (2005) 923

$H_2(r,v)$ generation mechanisms

By electrons: e-v excitation of H_2 by electrons (H_2^- as intermediate)
E-v excitation of H_2 by e through high excited states H_2^{**}
high T_e required & no J excitation?!

By dissociative recombination of H_3^+ by cool electrons (25 % only)
$H_3^+ + e \rightarrow H_2(r,v) + H$ and $H + H + H$ (75%) J excitation!

By associative attachment $H^- + H \rightarrow H_2(r,v) + e$ J excitation!

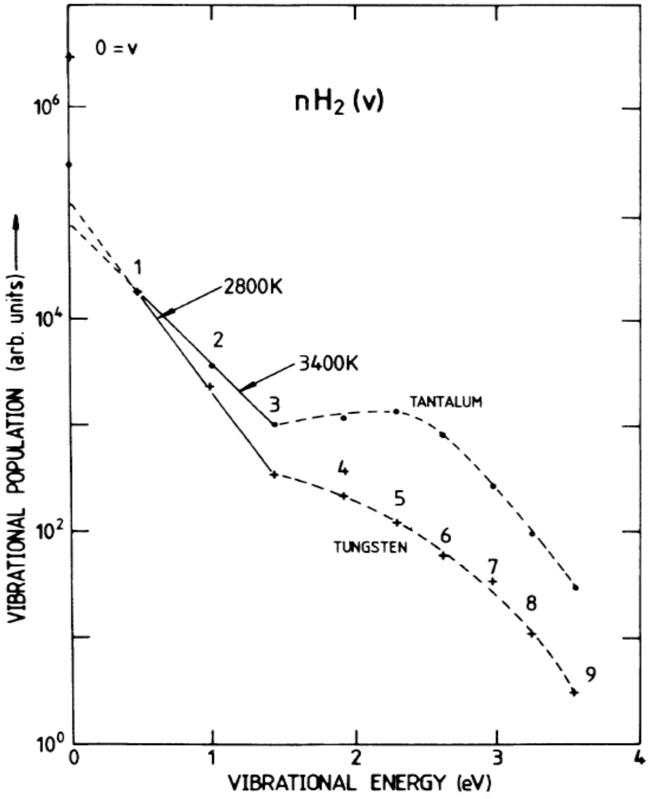
By surface association: $H(s) + H \rightarrow H_2(r,v) + e$ J excitation!
As H atom production is largest chemical reservoir this is potentially strongest source of $H_2(r,v)$

Re-distribution by collisions in volume: by electrons, by H , by H_2
and by repetitive $H_2(r,v) + e \leftrightarrow H- + H$

$H_2(r,v)$ generation at surface in past

Surface excitation is possible even at low fluxes

Hall 1988 (Hot filament) [1]:



R.I. Hall, I. Cadez, M. Landau, F. Pichou, C. Scherman, Phys. Rev. Lett., 60, 337 (1988)

$H_2(r,v)$ re-distribution

Re-distribution by collisions in volume: by electrons, by H , by H_2 and by repetitive $H_2(r,v) + e \leftrightarrow H^- + H$

By electrons: most probable with small $\Delta J = \pm 2$, highest for high J:
→ ladder climbing in J faster at high J, + vibration excitation
→ Low J states effectively coupled by H, H_2 collisions
→ multiple hockey stick?

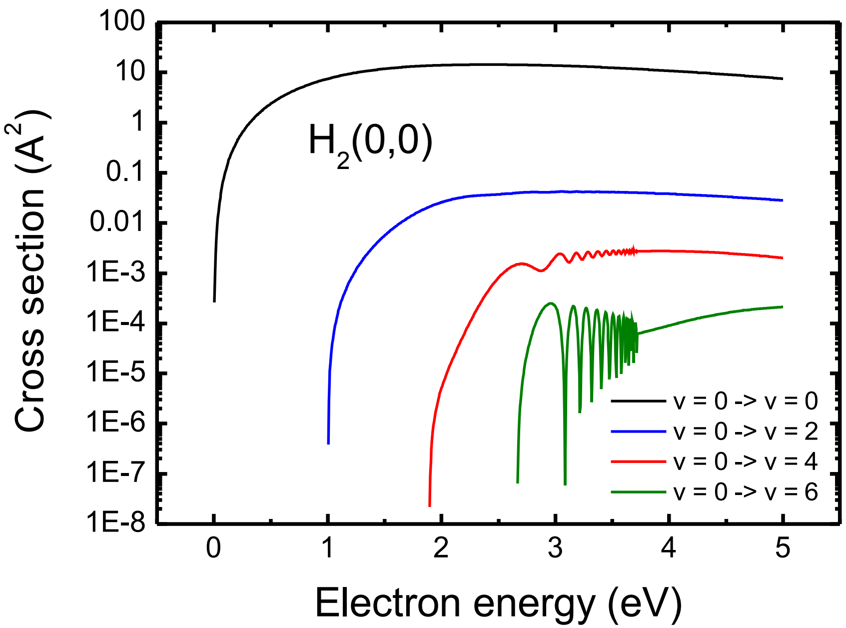
Re-distribution by heavy particle collisions: by H atoms?!
Only limited cross section data, but again same principle, but with $\Delta E \sim 0$
→ If $\Delta J = - 2$ then $\Delta v = + 1$ at higher v, etc

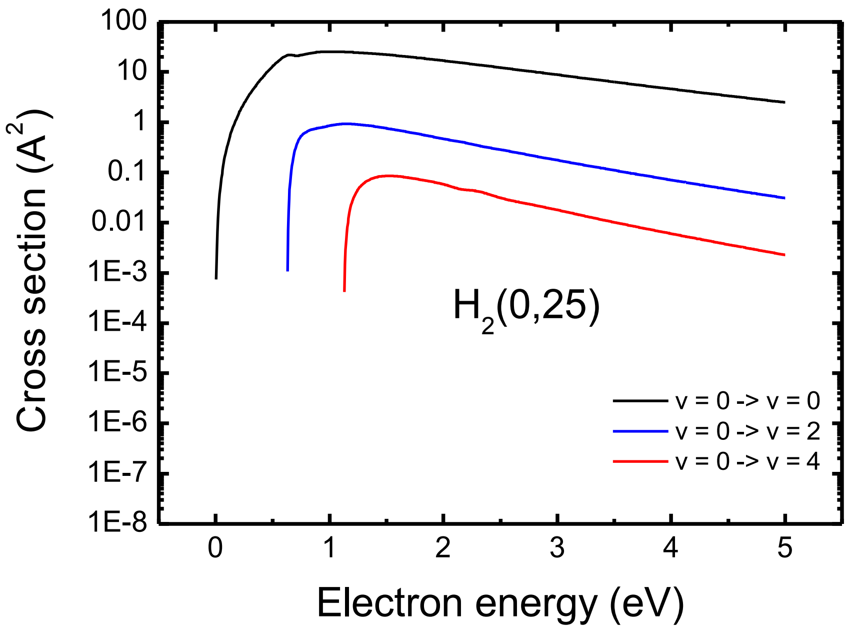
Re-distribution by $H^- + H \leftrightarrow H_2(r,v)$ populates higher J states with preference

Excitation by electron collisions

$$H_2(v,J) + e \rightarrow H_2(v',J') + e$$

$$\Delta J = \pm 2 \ (\pm 4,\ldots)$$





-> cross sections larger for excitations in high rotational levels.

Horacek, J.; Cizek, M.; Houfek, K.; Kolorenc, P. & Domcke, W.
Dissociative electron attachment and vibrational excitation of H2 by low-energy electrons: Calculations based on an improved nonlocal resonance model. II. Vibrational excitation
Phys. Rev. A, **2006**, *74*, 022701

Comparision rate coefficients

VE process:

$H_2(v,J) + e \rightarrow H_2(v',J') + e$ $\quad k_{max} = 1.0 \cdot 10^{-13}\ m^{-3}s^{-1}$ (0,27) → (0,29)

$\quad k_{min} = 7.4 \cdot 10^{-22}\ m^{-3}s^{-1}$ (0,0) → (8,2)

DA process:

$H_2(v,J) + e \rightarrow H + H^-$ $\quad k_{max} = 2.4 \cdot 10^{-14}\ m^{-3}s^{-1}$ (0,31)

$\quad k_{min} = 6.7 \cdot 10^{-21}\ m^{-3}s^{-1}$ (0,0)

AD process:.

$H + H^- \rightarrow H_2(v,J)$ $\quad k_{max} = 5.0 \cdot 10^{-17}\ m^{-3}s^{-1}$ (2,22)

$\quad k_{min} = 2.6 \cdot 10^{-23}\ m^{-3}s^{-1}$ (0,0)

Only $v \leq 1$ and $J \leq 15$:

Collisions with H:.

$H_2(v,J) + H \rightarrow H_2(v',J') + H$ $\quad k_{max} = 7.4 \cdot 10^{-17}\ m^{-3}s^{-1}$ (1,3) → (1,1)

$\quad k_{min} = 4.0 \cdot 10^{-22}\ m^{-3}s^{-1}$ (0,16) → (1,0)

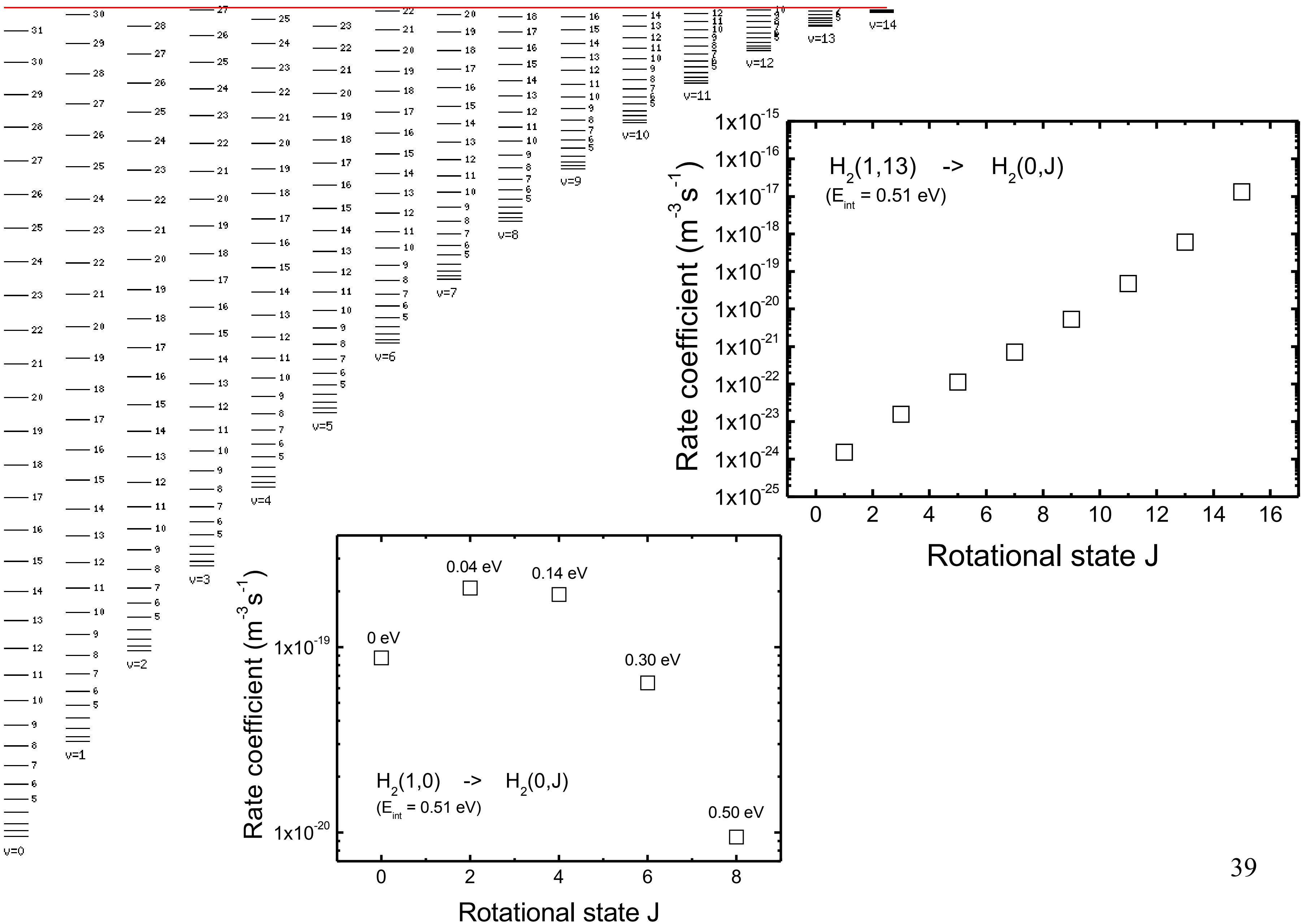
Collisions with H_2(0,0):.

$H_2(v,J) + H_2(0,0) \rightarrow H_2(v',J') + H_2(0,0)$ $\quad k_{max} = 6.6 \cdot 10^{-17}\ m^{-3}s^{-1}$ (1,3) → (1,1)

$\quad k_{min} = 1.8 \cdot 10^{-25}\ m^{-3}s^{-1}$ (0,15) → (0,1)

(5000 K for hydrogen atoms and molecules / 10 000 K for electrons)

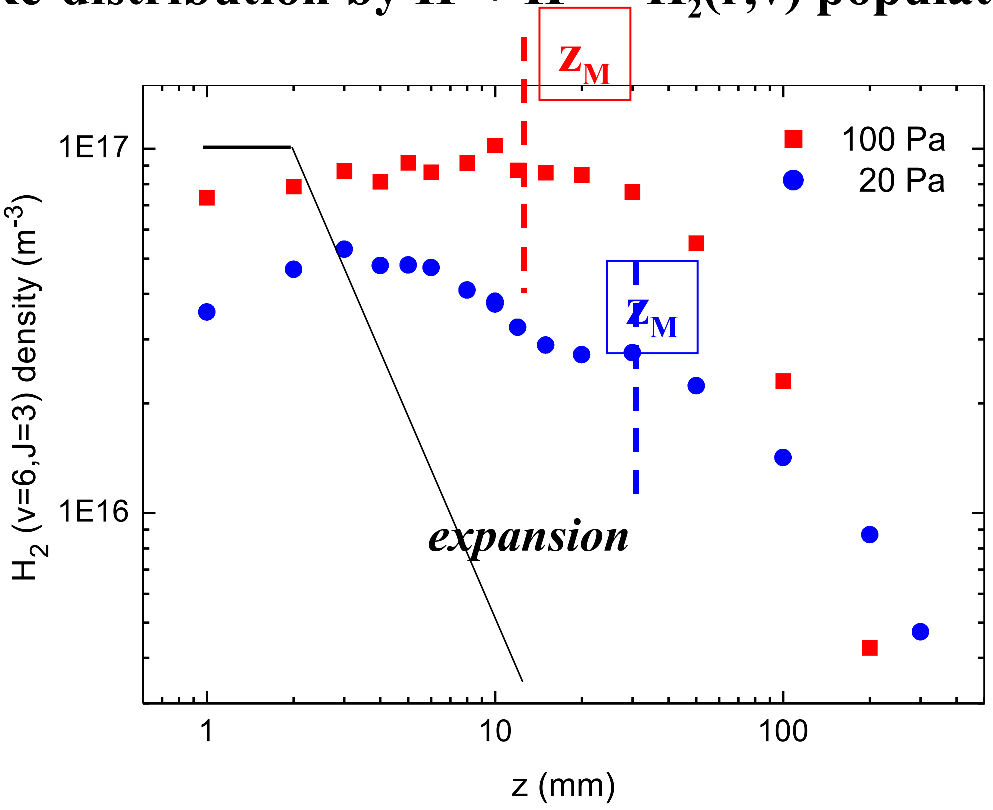
Rate coefficient H collisions



$H_2(r,v)$ re-distribution, z dependence

Re-distribution by heavy particle collisions: by H atoms?!
Only limited cross section data, but again same principle, but with $\Delta E \sim 0$
→ If $\Delta J = -2$ then $\Delta v = +1$ at higher v, etc

Re-distribution by $H^- + H \leftrightarrow H_2(r,v)$ populates higher J states with preference



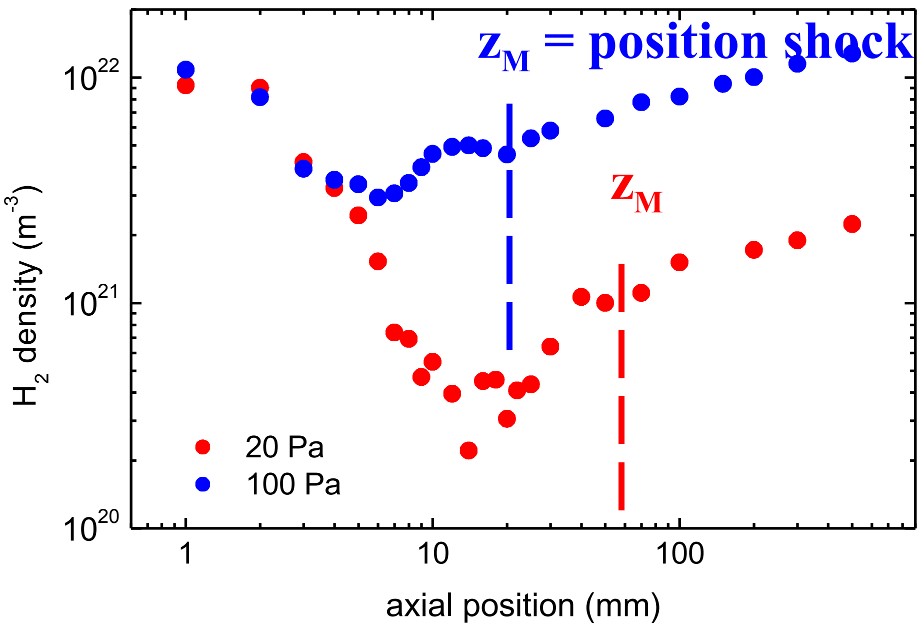
- **z up to shock at z_M:**
- **$n(H_2(3,6)$ does not decrease despite expansion**
- **generation? At front surface?**

- **z after shock at z_M:**
  decrease by de-population
  fast decrease by collisions H and H_2(, low J)

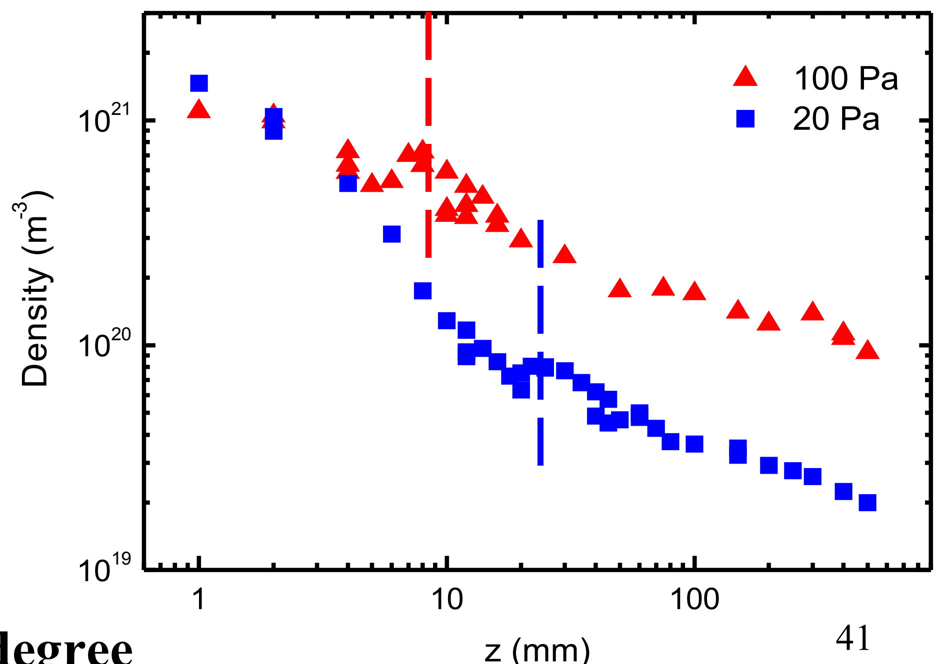
Expansion: z dependence: $1/z^2$ density

$n(H_2)$ Rayleigh scattering

H_2 density follows $1/z^2$ law



n(H) Two photon LIF (TALIF)



H density weaker z-dependence
→ reflected H atoms?

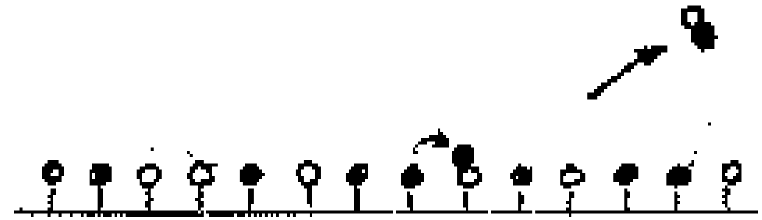
→ apparent increasing dissociation degree

Surface mechanisms

H flux large: surface H passivated (& in metal): 3 processes:

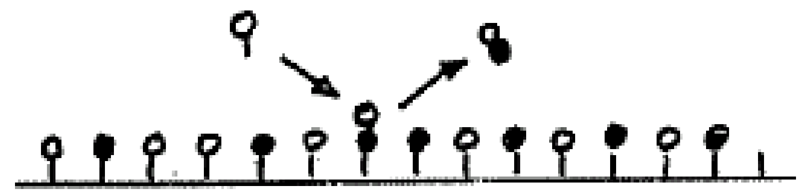
Langmuir Hinshelwood (LH)

2 atoms at surface associate



Eley Rideal(ER)

incoming atom picks up atom



→?Additional absorption:

weakly bond atoms on passivated surface

direct pick up (~ hot ER)

reaction (~ hot LH)

In plasmas: large radical fluxes, low T & p: only last two operational?

Production $H_2(r,v)$ at surface

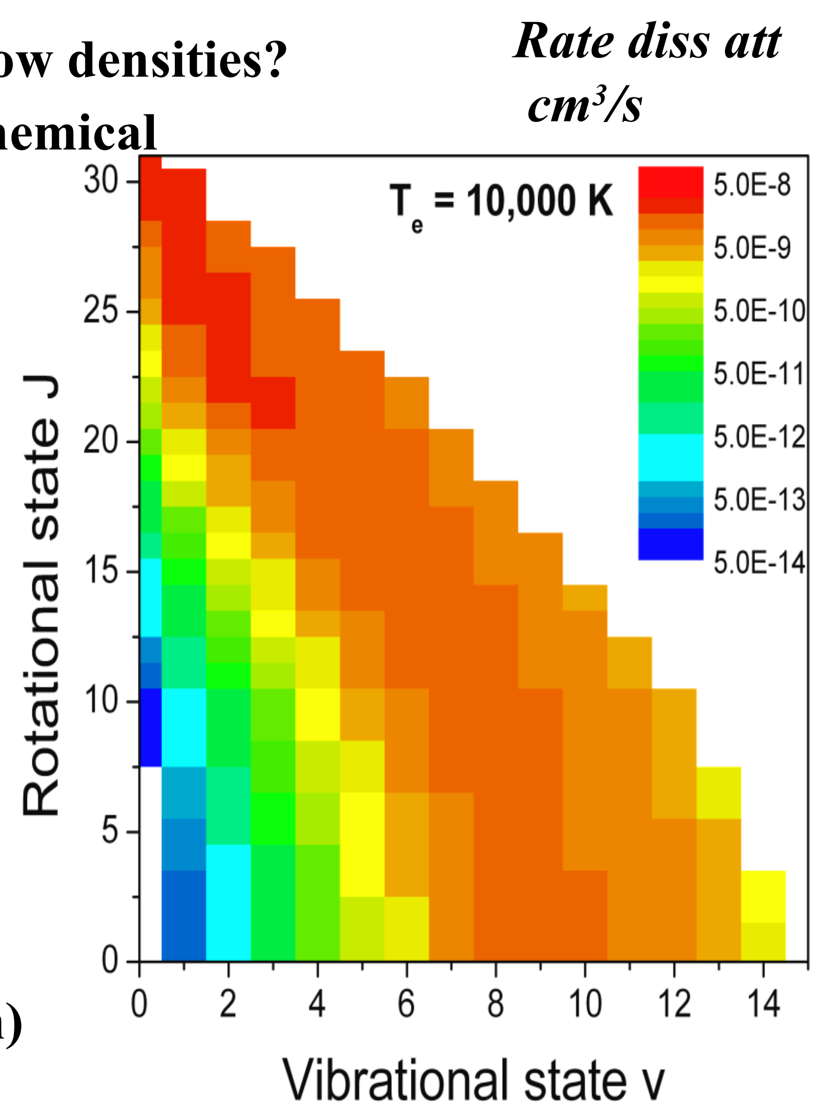
→?Additional absorption:
weakly bond atoms on passivated surface

direct pick up (~ hot ER)
reaction (~ hot LH)

In plasmas: large radical fluxes, low T & p: only last two operational?

Consequences of $H_2(r,v)$

Plasma chemistry:
More $H_2(r,v)$ than H atoms? especially at low densities?
$H_2(r,v)$ more important than H atoms as chemical



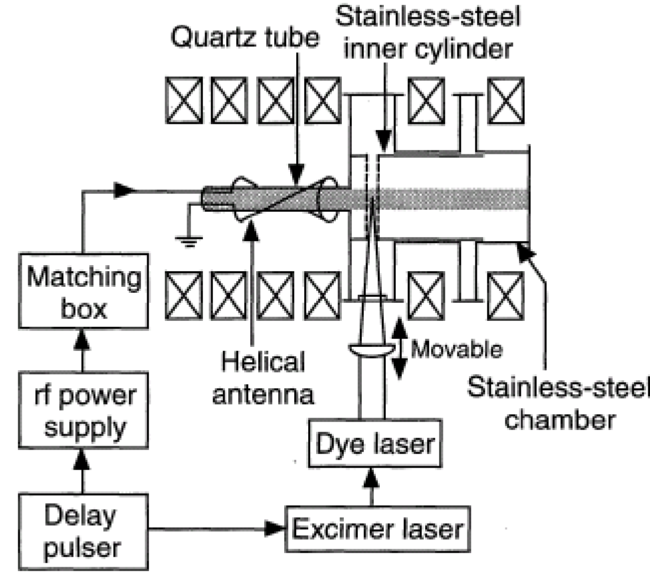
Negative ion formation:
Much more rate (and g) for high J

But still

More $H_2(r,v)$ means more H^- ions!
especially at low densities, H^- ions survive long enough to be extracted?
Note: at moderate n_e, even at high production rates of H^-, H^- life time is short (mutual recombination) and thus H^- density is low.

Mechanism: t-dependent studies in $O + O \rightarrow O_2$

Surface mechanisms: O + O → O_2

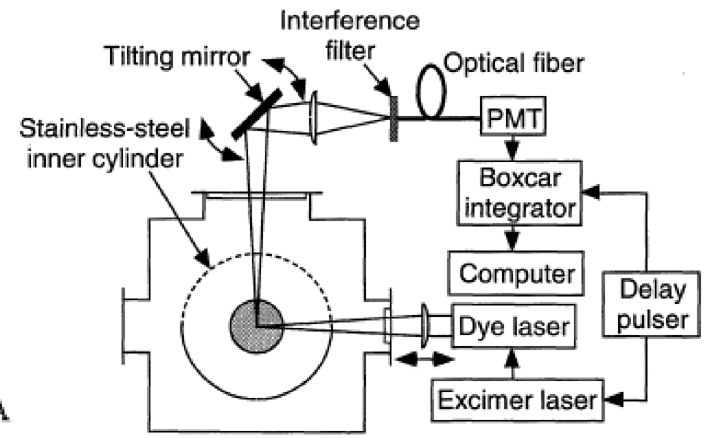


Pulsed helicon discharge in O_2 at low p: 4 Pa
1 kW @ 13.56 MHz, 1 kG field

Short pulse: O production < 1 monolayer
$\tau_{pulse} < \tau_{coverage}$

Long pulse: O production >> 1 monolayer
$\tau_{pulse} > \tau_{coverage}$

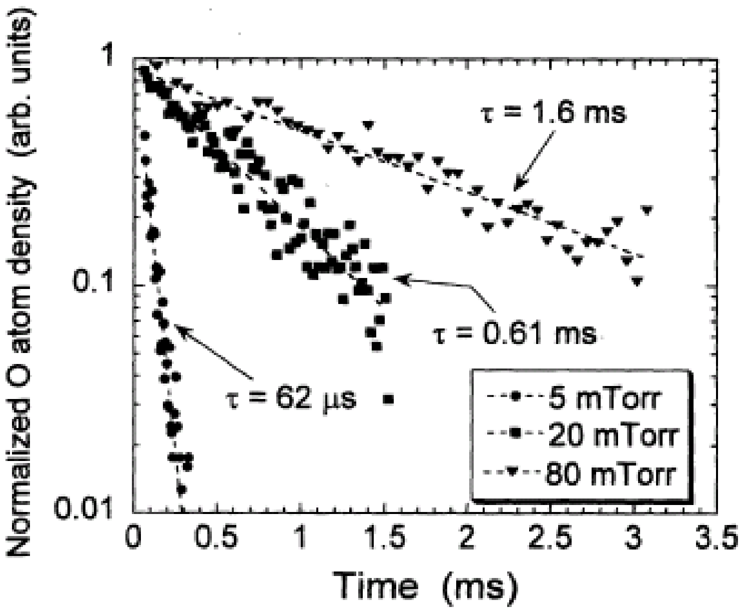
Measurement with TALIF of O density (t):



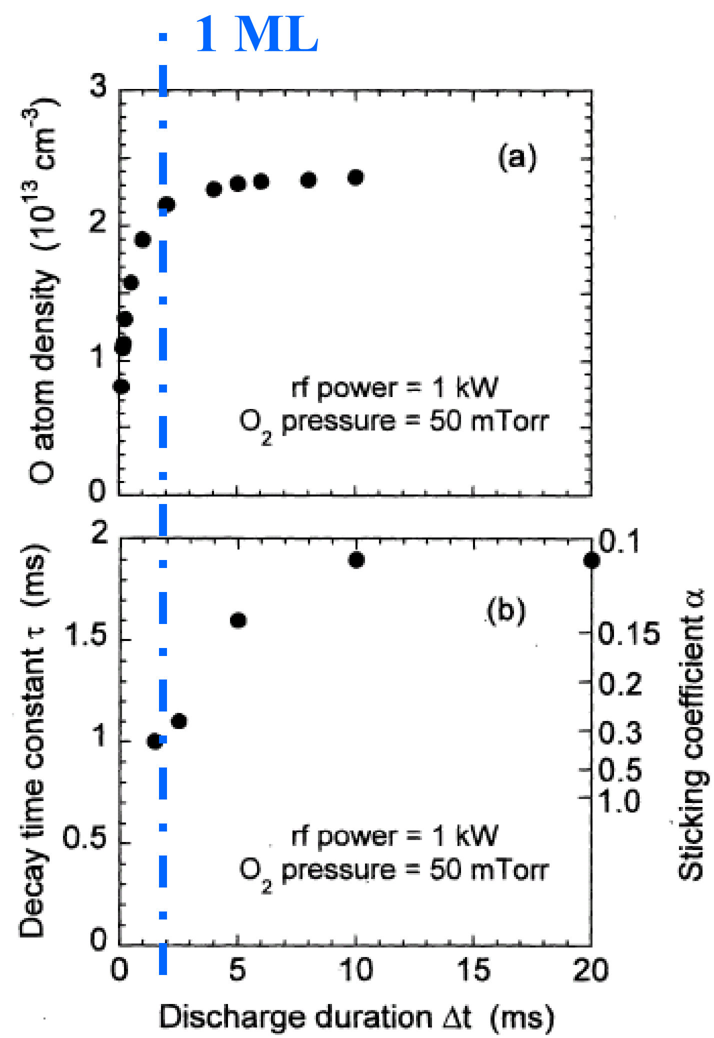
Short pulse: low O, short life time
Long pulse: high O, long life time

Jun MATSUSHITA*[1], Koichi SASAKI*[2] and Kiyoshi KADOTA
Jpn. J. Appl. Phys. Vol. 36 (1997) pp. 4747–4751

Surface mechanisms: $O + O \rightarrow O_2$



Dependence on p:
O life time ↔ diffusion to surface
Loss O: association to O_2 at surface



O density increases with duration plasma:
for duration > 2 msec: full coverage!

Sticking coefficient decreases from:
γ ~ 1 for low coverage
to
γ ~ .12 for full coverage:
Chemistry different on fully vovered stainless steel surface

Mechanism O + O → O_2 at surface

For a short time < $\tau_{coverage}$ the surface is filled with one monolayer O atoms

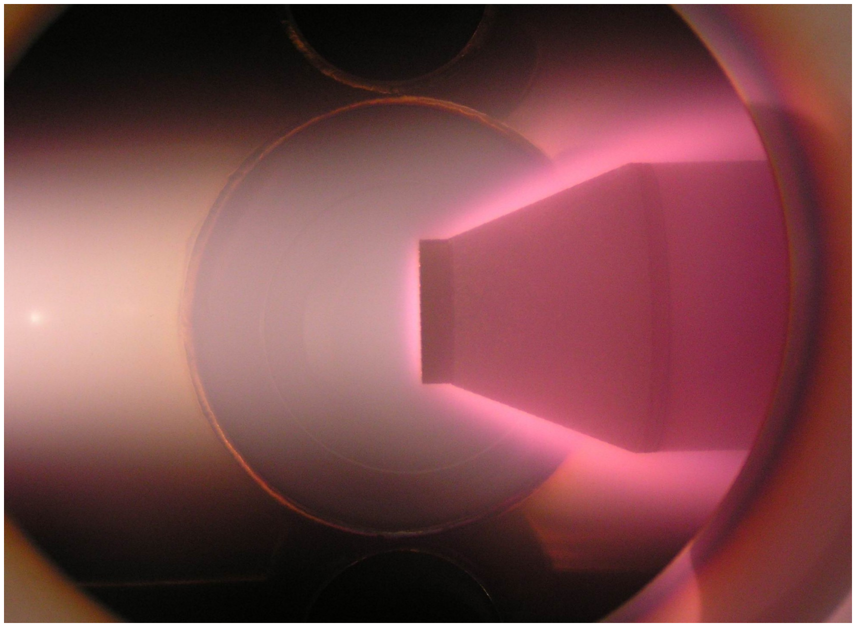
Then passivated?

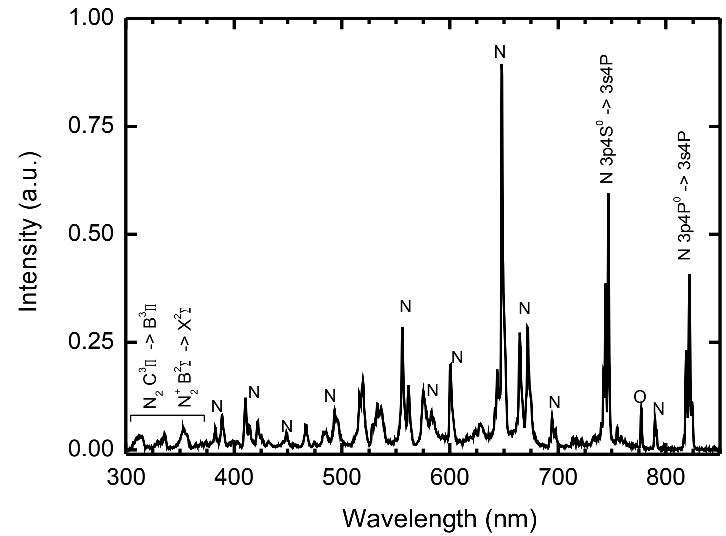
New O atoms in less bound states?Higher chance of reflection

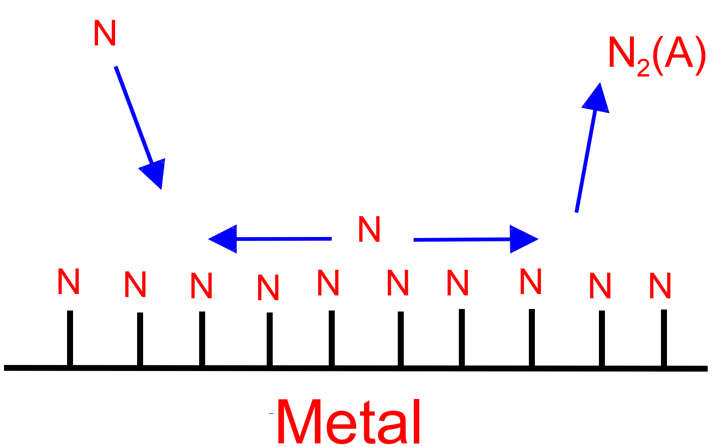
γ lower!! Depends on flux O atoms?

Excitation: there are signs of significant O_2* production at surface

N_2^* production at surface

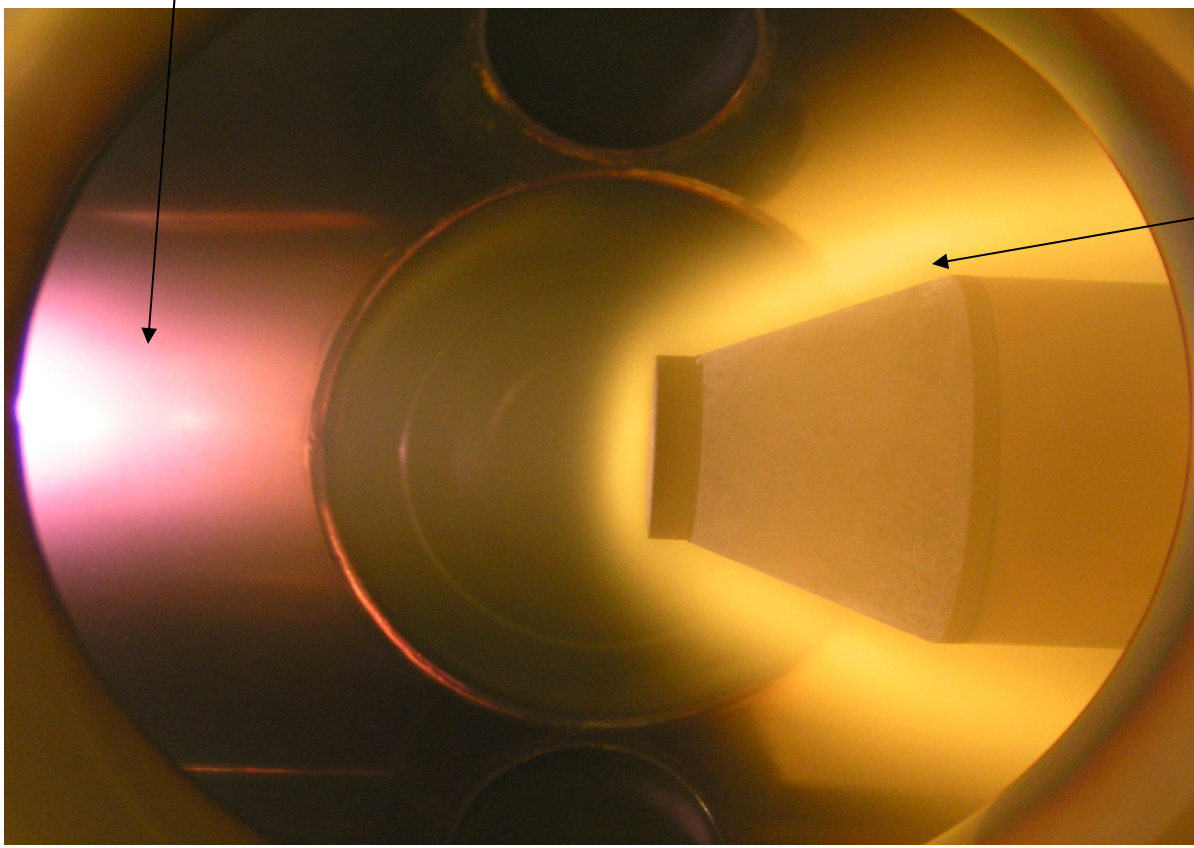






N/O: NO_2* generation

N_2 (B→A), N_2^+(B→X), N lines

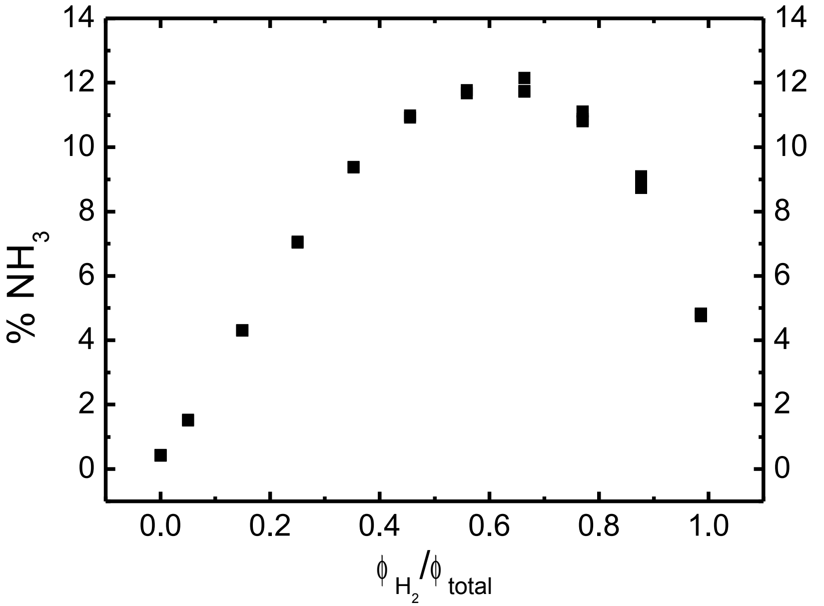


NO_2

NH_3 formation at surface from N_2/H_2 plasmas

Ammonia formation in:
-- Ar^+/e plasmas with N_2/H_2 in background → N & H radicals

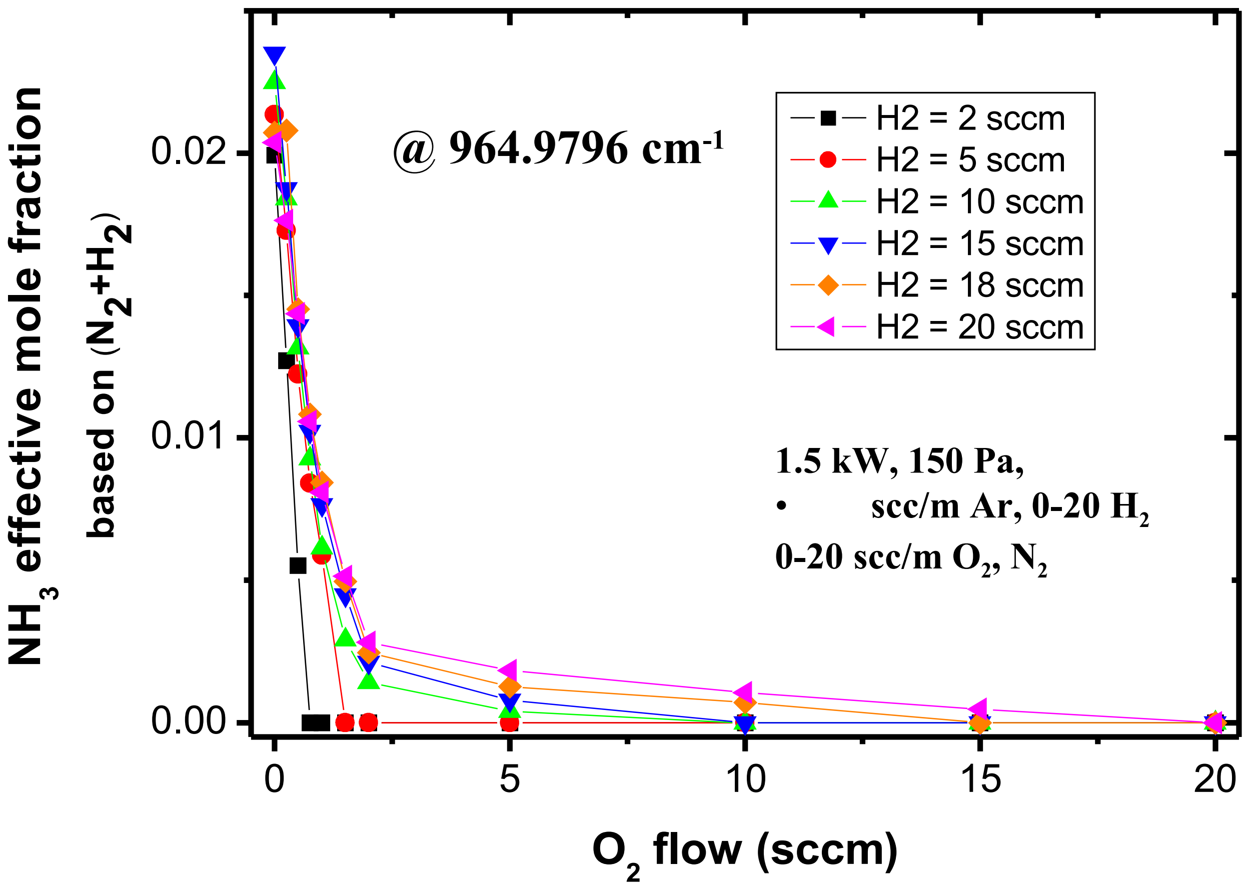
-- N_2/H_2 source: here reaction
- $N + H_2 \rightarrow NH + H$
- NH, H, (N) radicals → surface



N/H radicals → surface with N, H, NH/NH_2 → N_2, H_2, NH_3

Efficiency can be high: if H small then near all H ends up in NH_3

NH_3 decreases with increasing O_2 microwave INP



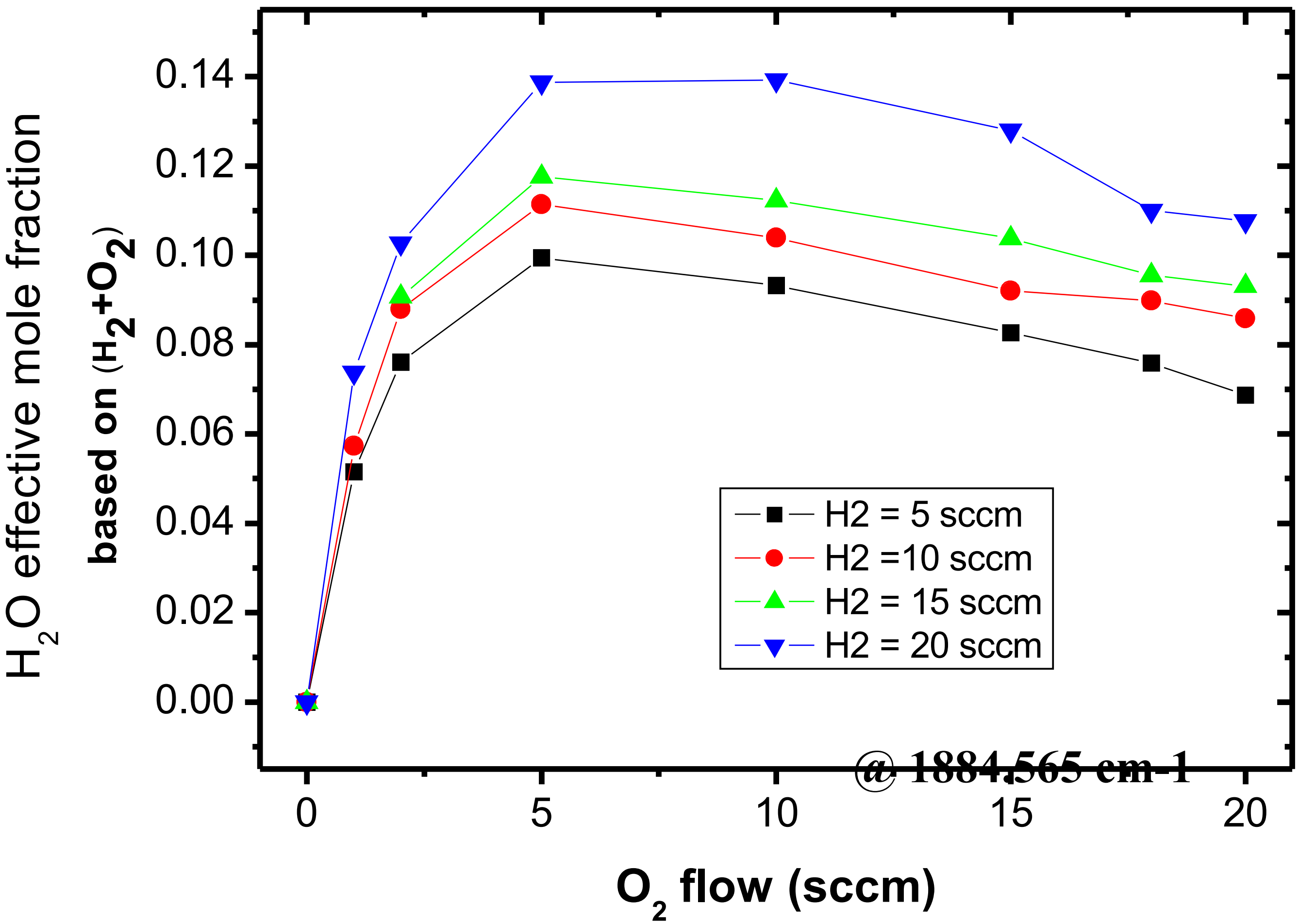
With O. Gabriel, J. Roepcke, S. Welzel, G. Stancu, G. Lombardini, INP Greifswald

mole fraction based on N_2 + H_2: NH_3: < 3-5 %

Very similar results: few % NH_3 with no O_2, strongly decreasing with O_2

Note: very different surface than in ETP: ss versus Aluminium + Quartz.

H_2O formation in N/H + O INP µw plasma



1.5 kW, 150 Pa,
- **scc/m Ar, 0-20 H_2**

0-20 scc/m O_2, N_2

Note: mole fraction based on $H_2 + O_2$: H_2O > 10 %; similar results in ETP-TU/e

very effective use of O for small O_2 flow

Summary molecule formation

- **In plasma large production of radicals → large radical flux**
  short surface coverage time, passivated surface

- **Surface association dominant mechanism for molecule formation:**
  H + H(s) → H_2(r,v), similarly N + N(s) → N_2(X,A?),

- **Surface occupation of precursors determine desorbed molecules:**
  NH_2(s) + H → NH_3; OH(s) + H → H_2O etc

- **Formation of H_2, N_2, CO, H_2O dominant**

  2e level: NO, NH_3, HCN, CH_4, C_nH_m

- **Also small organic molecules: H_2CO, CH_3OH, CHOOH**

Conclusions

- Expanding thermal plasma very promising: bright source: Ar^+, H^+, H, N…
- Possibility to dissociate each injected molecule within residence time
- Enormous fluxes: passivated surfaces, surface generation of excited molecules
- In H_2 efficient dissociation and formation $H_2(r,v)$ from less bound states?
- $H_2(r,v)$ molecules formed at surface: helps H^- formation
- Scaled down & with low pressure: promising for H^- source
- Formation of other molecules mostly at surface: N_2, O_2, NH_3, NOx, H_2O, CO...
- Adsorbed fragments at passivated surface: NH_2, OH, N, H….
- Molecule formation: more "chemical", temperature & abundances (in radicals)

Motivation

- **Influence of surface in generation of (excited?!) molecules? $H_2(r,v)$**
- **Influence of these molecules on process: H atoms → $H_2(r,v)$ → H^- ions**
- **Mechanisms of deposition, etching, surface modification, oxidation……**
- **Efficiency of molecule formation, H_2, N_2, NO, NH_3, CO, C_2H_2, CH_3OH…..**
- **Mechanisms of molecule formation in interstellar matter: H_2, NH_3, CH_3OH**
- **Importance negative ions, negative ion sources sources?**

- **Has there been enough done in plasma physics to get the ultimate material?**
- **Has there been enough effort to get the ultimate effort to obtain e.g. H^-?**

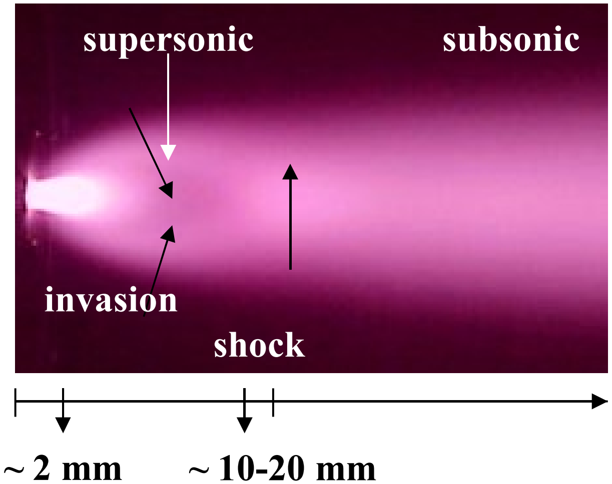
Invasion of H_2 in expansion of H/H_2

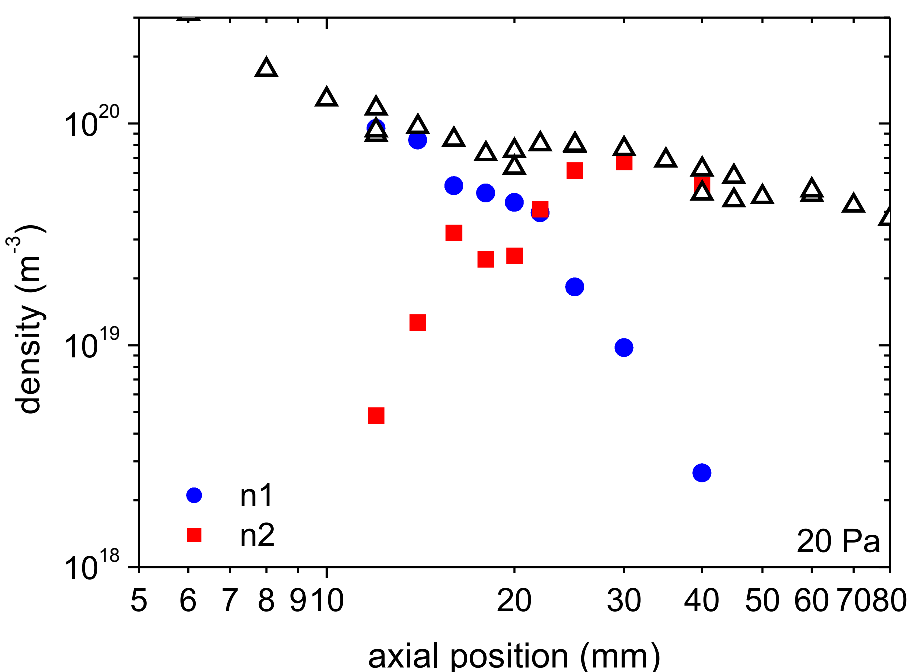
Scattering in of warm H_2 from outside by collision with supersonic H → slowed down H atom

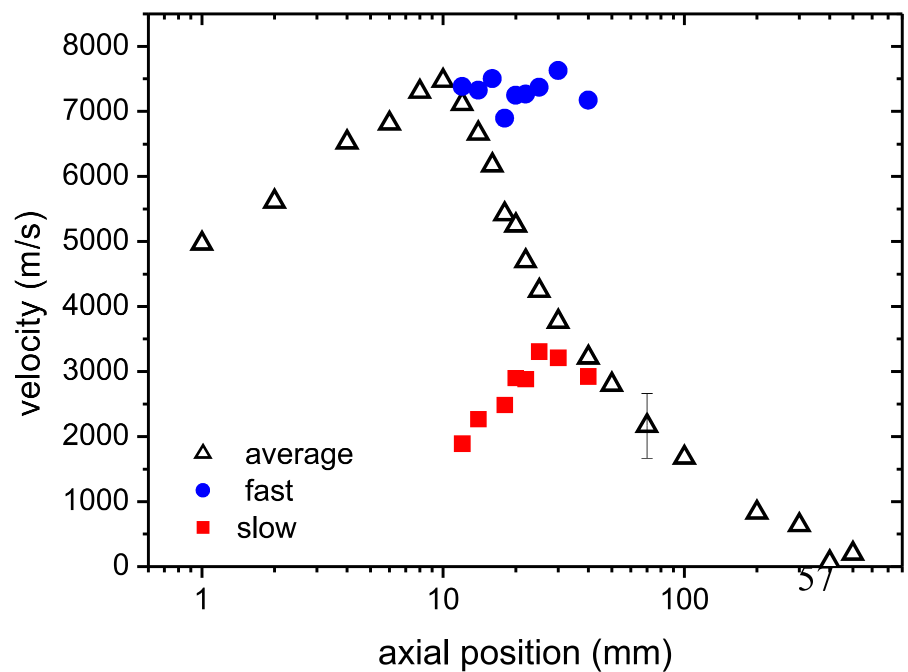
Measured H distribution: 2 components:

fast/cold (not collided yet) & slow/warm (collided)

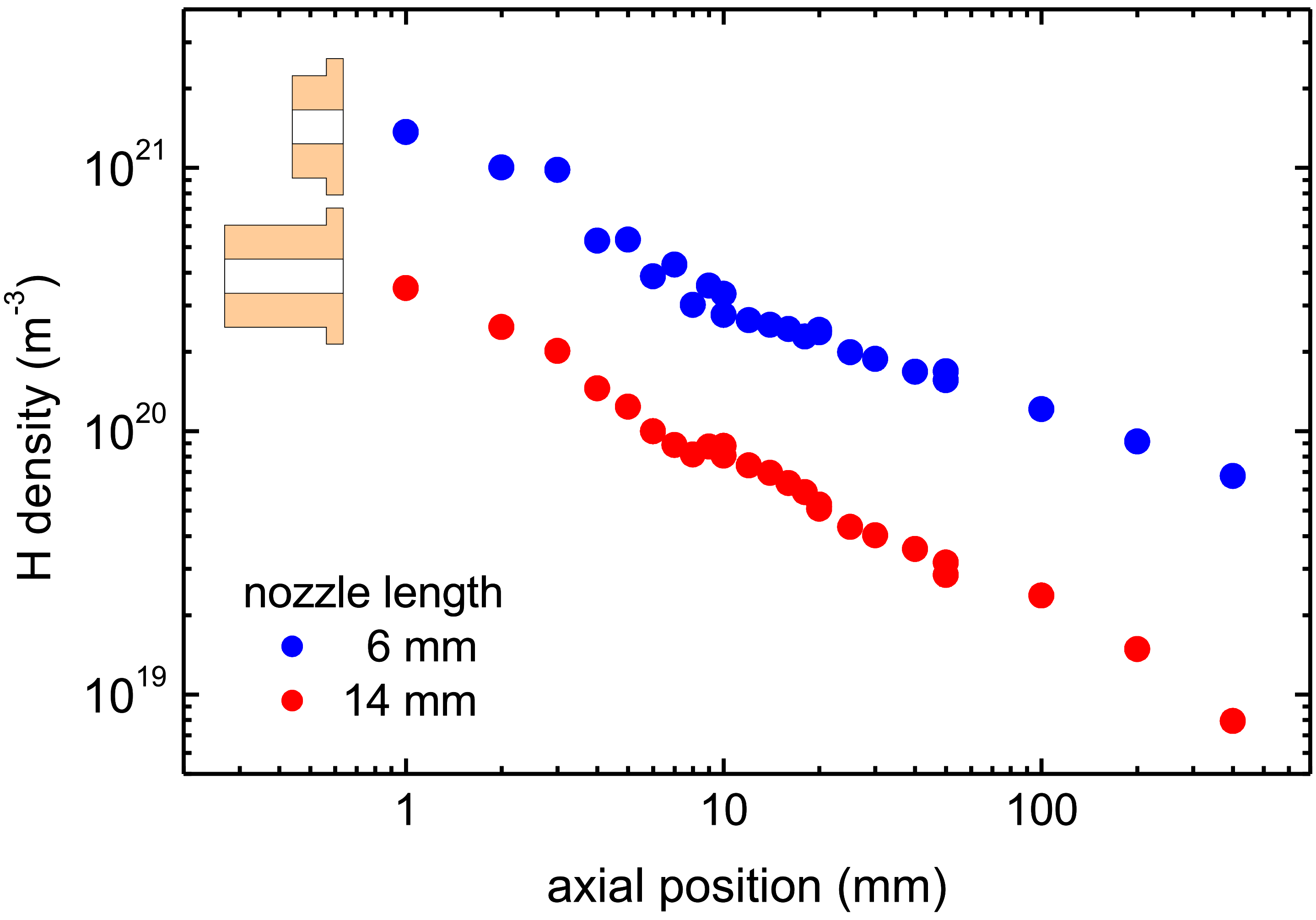
Both H distributions move radially out (H_2 moves in!)





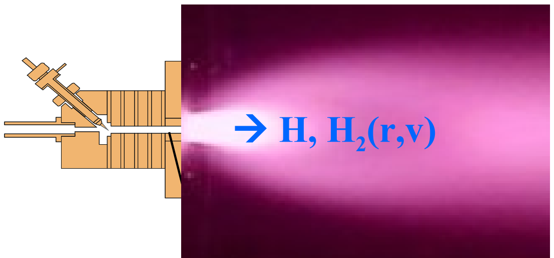


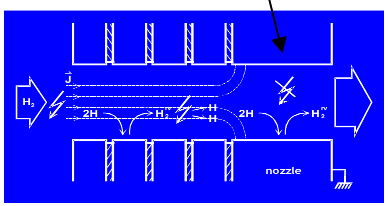
Effect of nozzle-length on H density



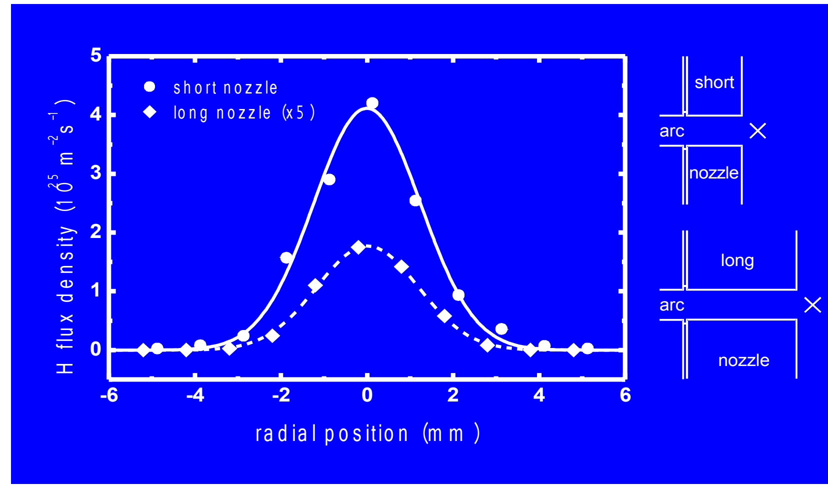
Mechanism of excited H_2(r,v) molecules formation

At nozzle surface: concluded from H increase for shorter nozzle length:





→ H, H_2(r,v)

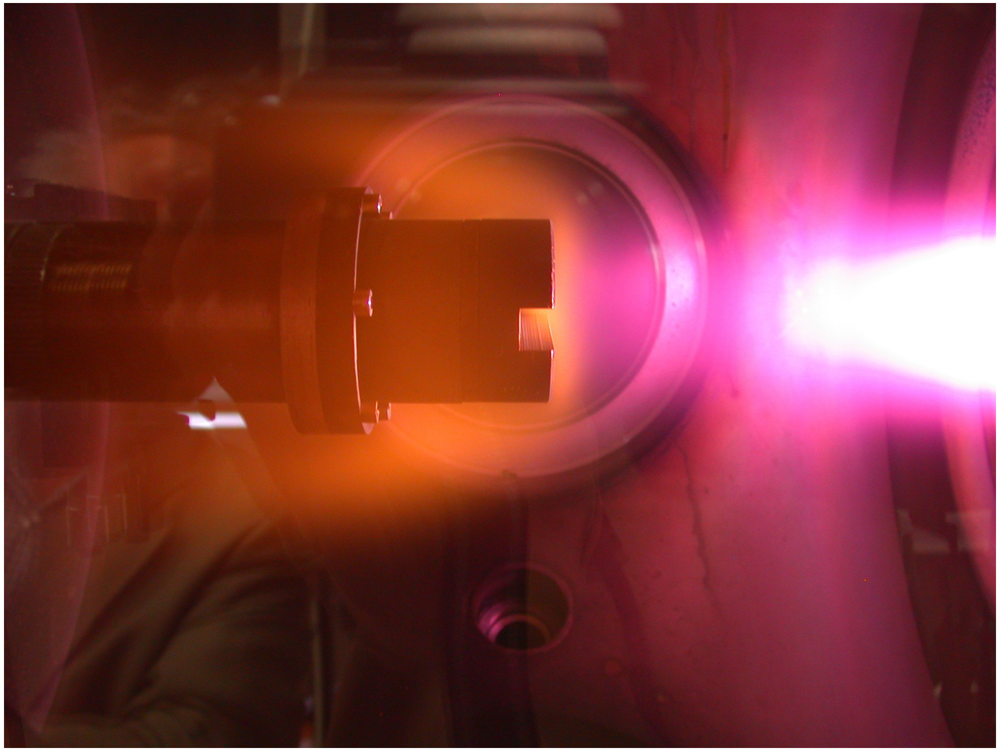


Nozzle surface → source of H_2(v,J):

Note: at nozzle surface: very high H flux: 10^{25}/s/m^2 ~ 10^6 MonoLayers /s
despite high surface T: H atom-passivated surface

Evidence excited products: O + N → surface → NO_2*

N/O to surface'
De-sorption excited fragments:
shuttle glow
If large fluxes N O atoms:
orange glow at substrate:
shuttle glow:



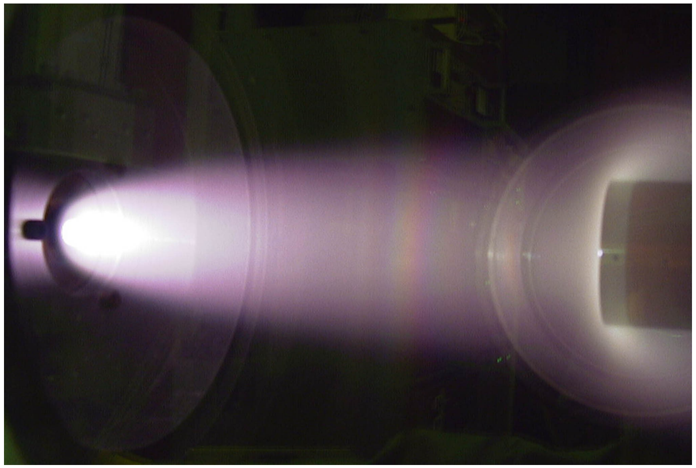
NO_2* desorption?

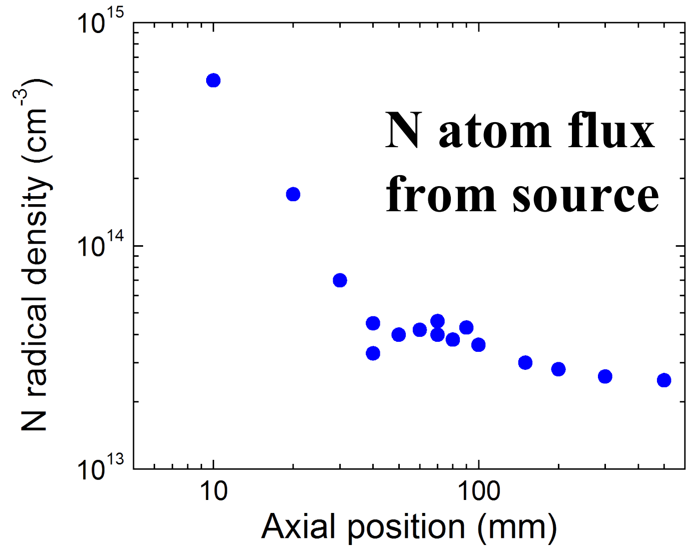
Generation of excited molecules

See also flow pattern

Proof of surface production, proof of excited molecules!
Speculation: negative ion formation?

Evidence excited products: Nitrogen N → N_2

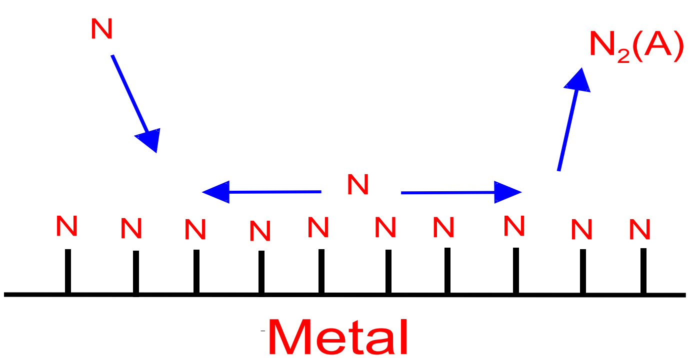




In volume: atoms/molecules = ratio time constants: $N/N_2 \sim \tau_N/\tau_{res} \sim 0.1$

At surface: more N than in volume

At surface (N covered)



N association at N passivated surface:

→Extra light: B→A & N_2^+(B-X),

→ low T_e (0.1eV),

new mechanism at large N flux?

: N + N → N_2(B, a, a'?)