The density of NH and NH_2 radicals in ammonia forming expanding plasmas

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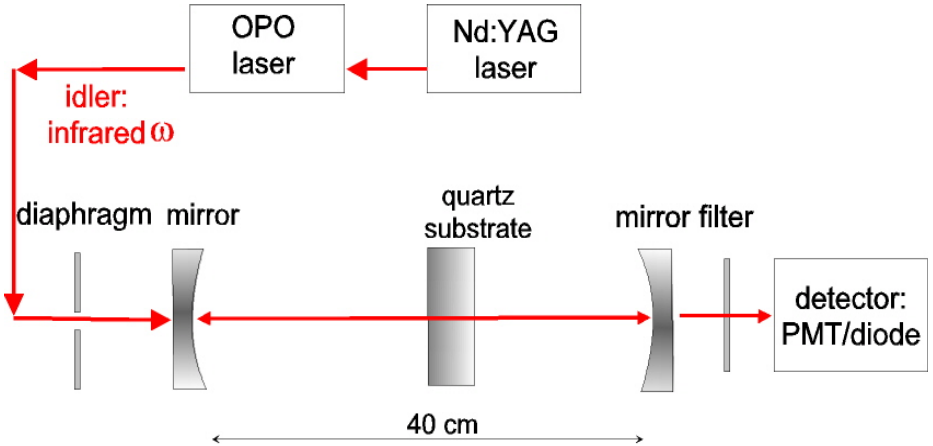
Outline

- Introduction
- Experimental setup
  - Expanding thermal plasma setup
  - Cavity ring-down spectroscopy system
- Spectroscopic information
  - NH and NH_2 Spectra
  - Rotational density distribution
- Results
  - NH and NH_2 densities
  - Plasma chemistry
- Conclusions

CRDS: a versatile technique

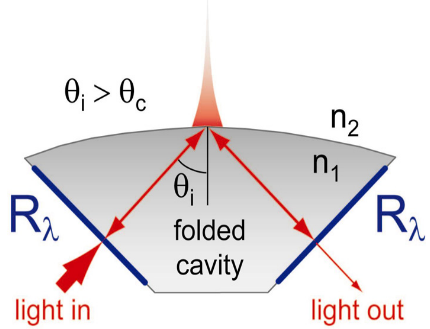
Cavity ringdown spectroscopy on:

- Gas phase radicals
- Thin films (tf-CRDS)



I.M.P. Aarts *et al*
APL **84,** 3079
(2004)

- Surface species (evanescent wave-CRDS)



A.C.R. Pipino *et al*
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Related techniques:

- Time resolved CRDS, Phase shift CRD, CEA

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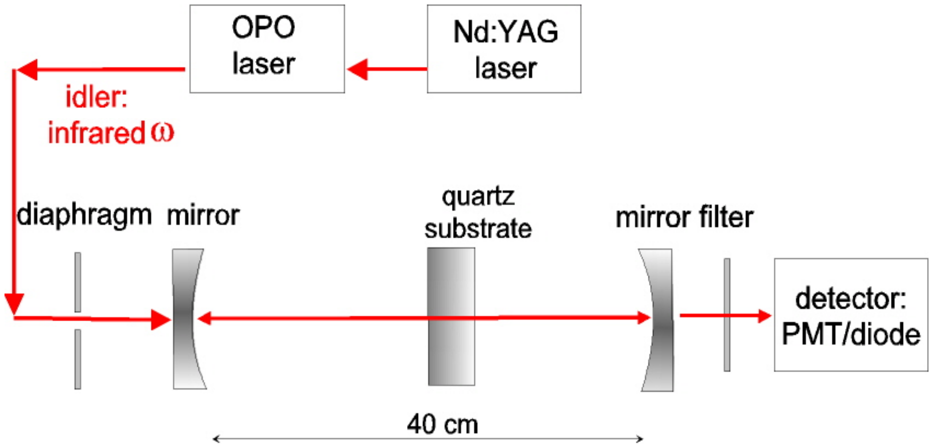

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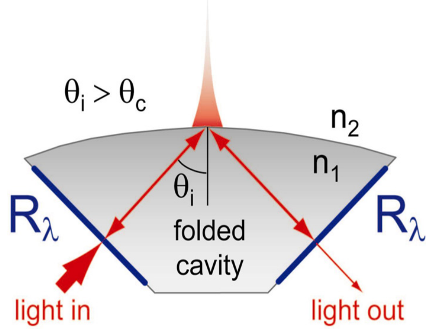

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Measured radicals and molecules

Particle	Used transition	λ (nm)
Si	$4s\ ^3P_1 \leftarrow 3p^2\ ^3P_0$	252
SiH	$A^2\Delta \leftarrow X^2\Pi(0 \leftarrow 0)Q_1(11.5)$	413
SiH_3	$\tilde{A}^2A_1 \leftarrow \tilde{X}^2A_1$ band	215 & 250
C	$3s\ ^1P_1 \leftarrow 3s\ ^1S_0$	248
C_2	$d^3\Pi_g \leftarrow a\ ^3\Pi_u\ (0 \leftarrow 0)$	517
CH	$A^2\Delta \leftarrow X^2\Pi(0 \leftarrow 0)$	431
CH_3	$\tilde{B}^2A_1 \leftarrow \tilde{X}^2A_2$ band	216
NH	$A^3\Pi \leftarrow X^3\Sigma^-(0 \leftarrow 0)P_{3,3}(9)$	340
NH_2	$\tilde{A}^2A_1 \leftarrow \tilde{X}^2B_1(090 \leftarrow 000)\Sigma^PQ_{1,7}$	597
NH_3	$\nu_1 + \nu_3$ combination band	1522

Growth a-Si:H (Si, SiH, SiH_3)

Growth a-C:H (C, C_2, CH, CH_3)

NH_3 generation/ NH_3 dissociation/ growth a-SiN_x:H (NH, NH_2, NH_3)

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CH_3	$\tilde{B}^2A_1 \leftarrow \tilde{X}^2A_2$ band	216
NH	$A^3\Pi \leftarrow X^3\Sigma^-(0 \leftarrow 0)P_{3,3}(9)$	340
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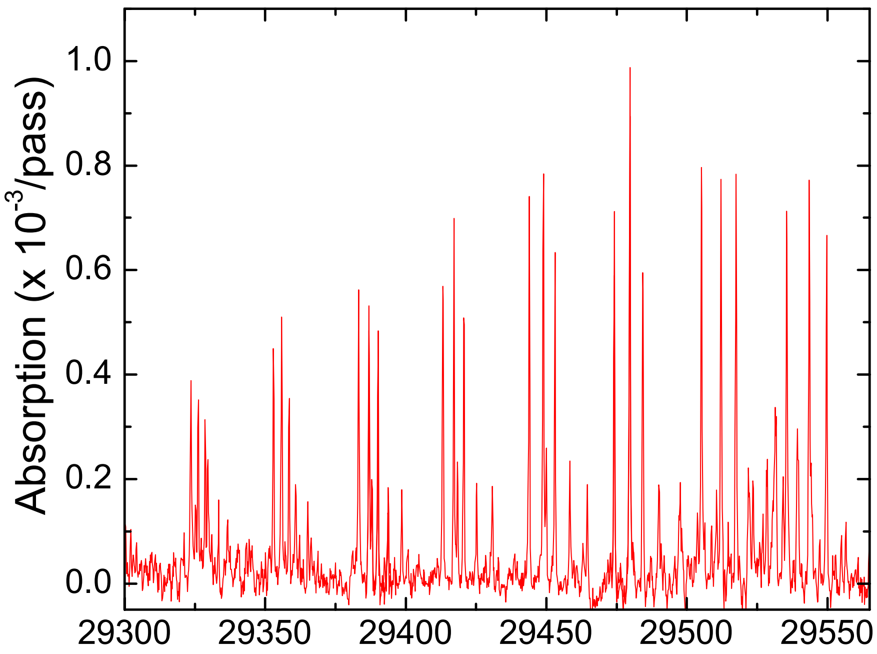
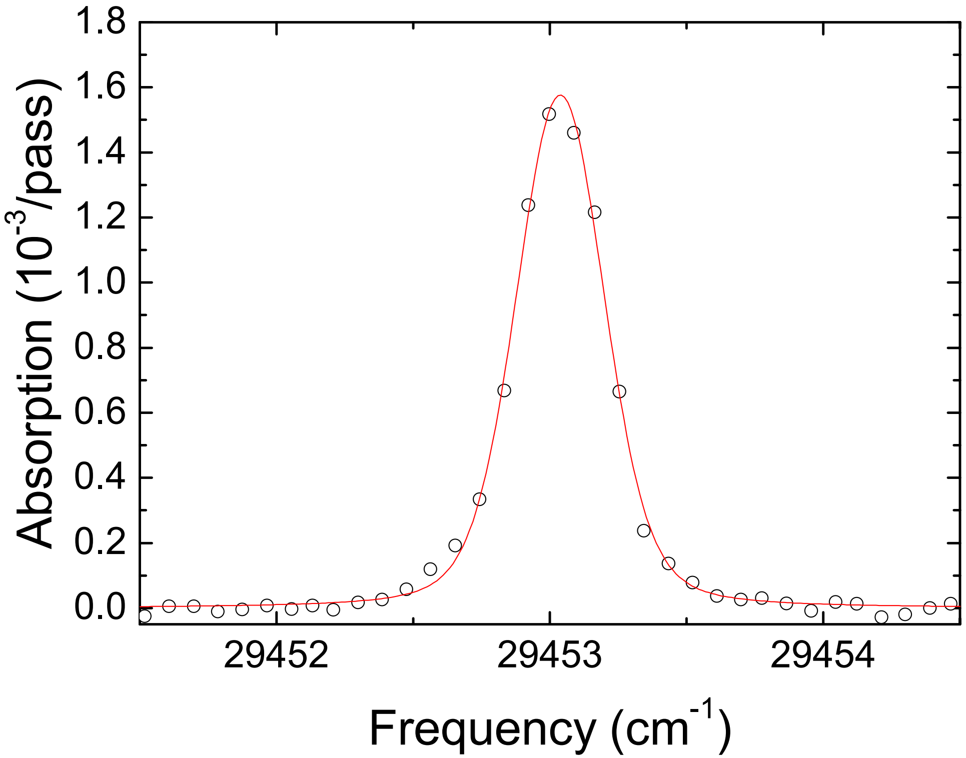
Relevant information from CRDS





1. Direct information:
   - — Kinetic temperature
   - — Rotational temperature
   - — Absolute densities
2. Secondary information
   - — Reaction rates
   - — (Plasma) Chemistry
   - — Relevance for surface processes

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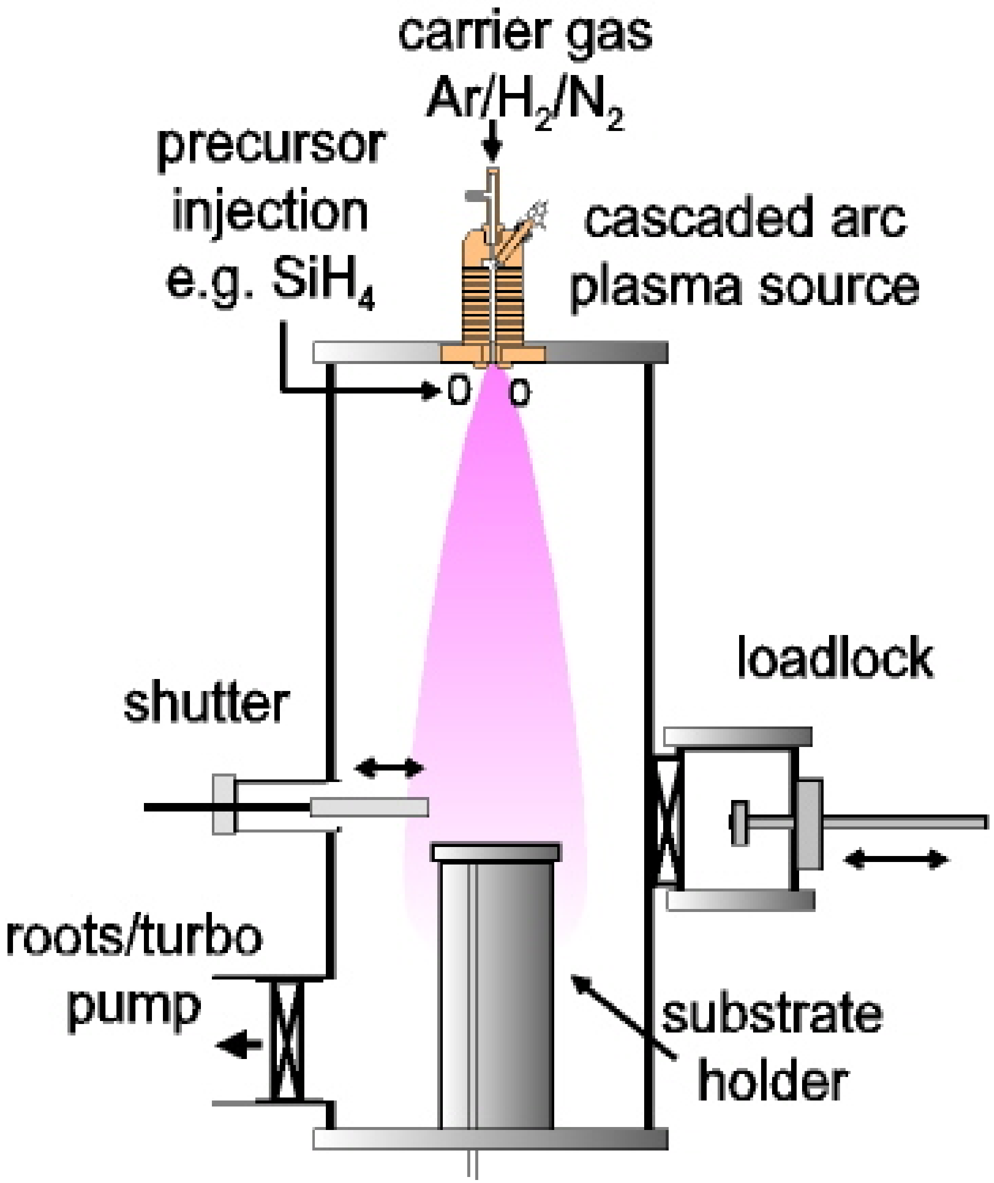
Expanding Thermal Plasma (ETP)



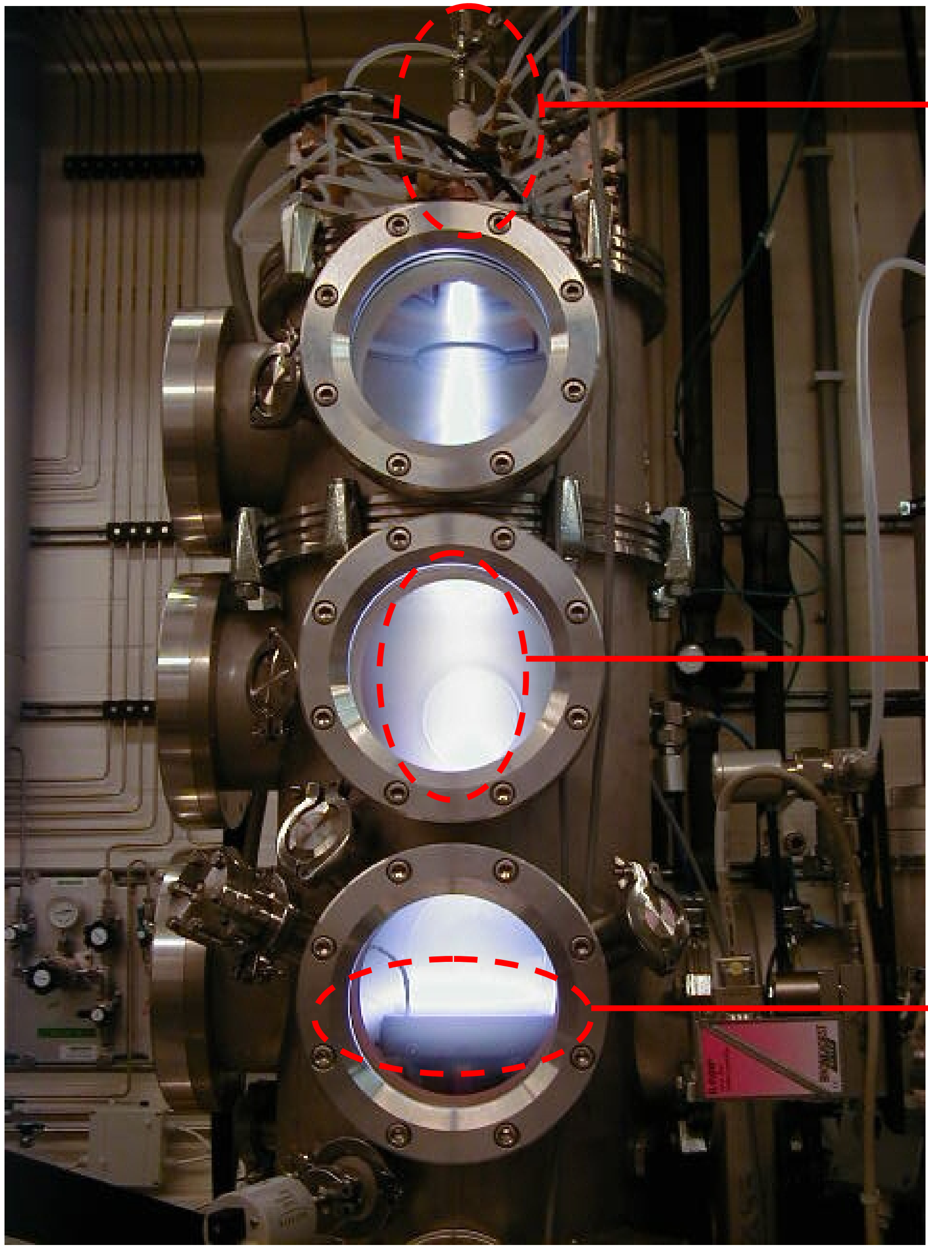
remote plasma

Plasma creation at high pressure (~0.4 bar)

Expansion to low pressure (~20 Pa) & precursor injection

(High-rate) deposition & no ion bombardment

Expanding Thermal Plasma (ETP)

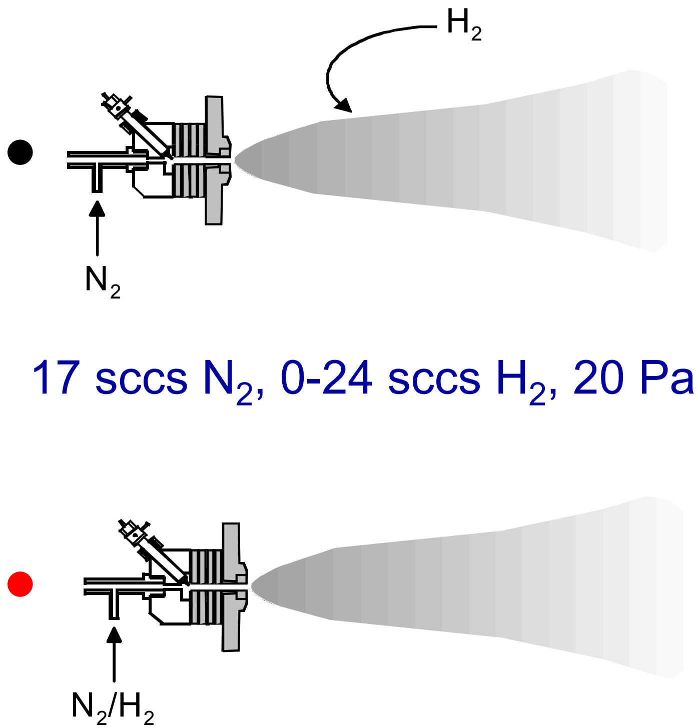


N_2/H_2
plasma creation

Plasma chemistry
leading to e.g. N, H, NH, NH_2, …

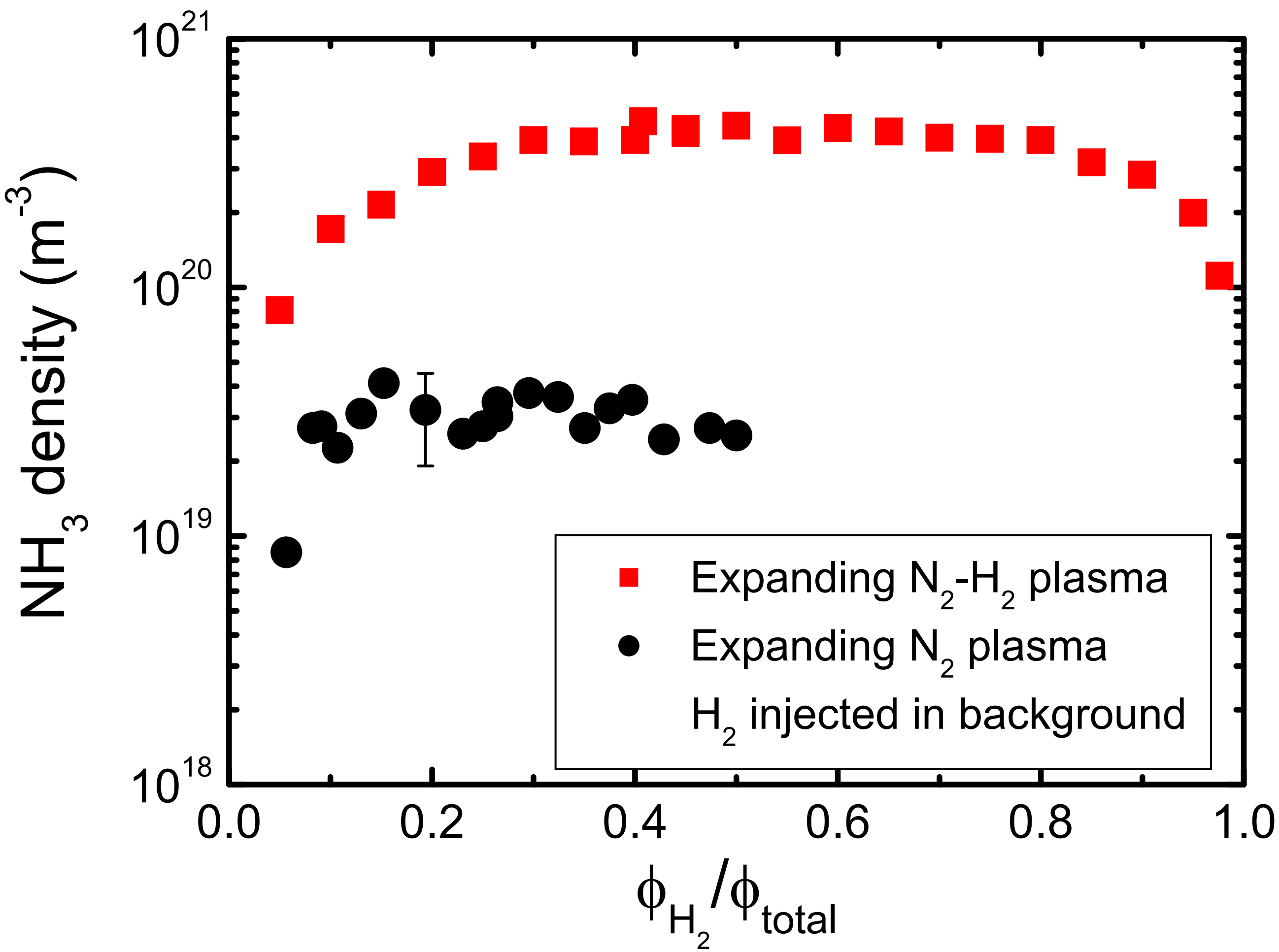
NH_3 formation

NH_3 densities in N_2-H_2 plasma



17 sccs N_2, 0-24 sccs H_2, 20 Pa

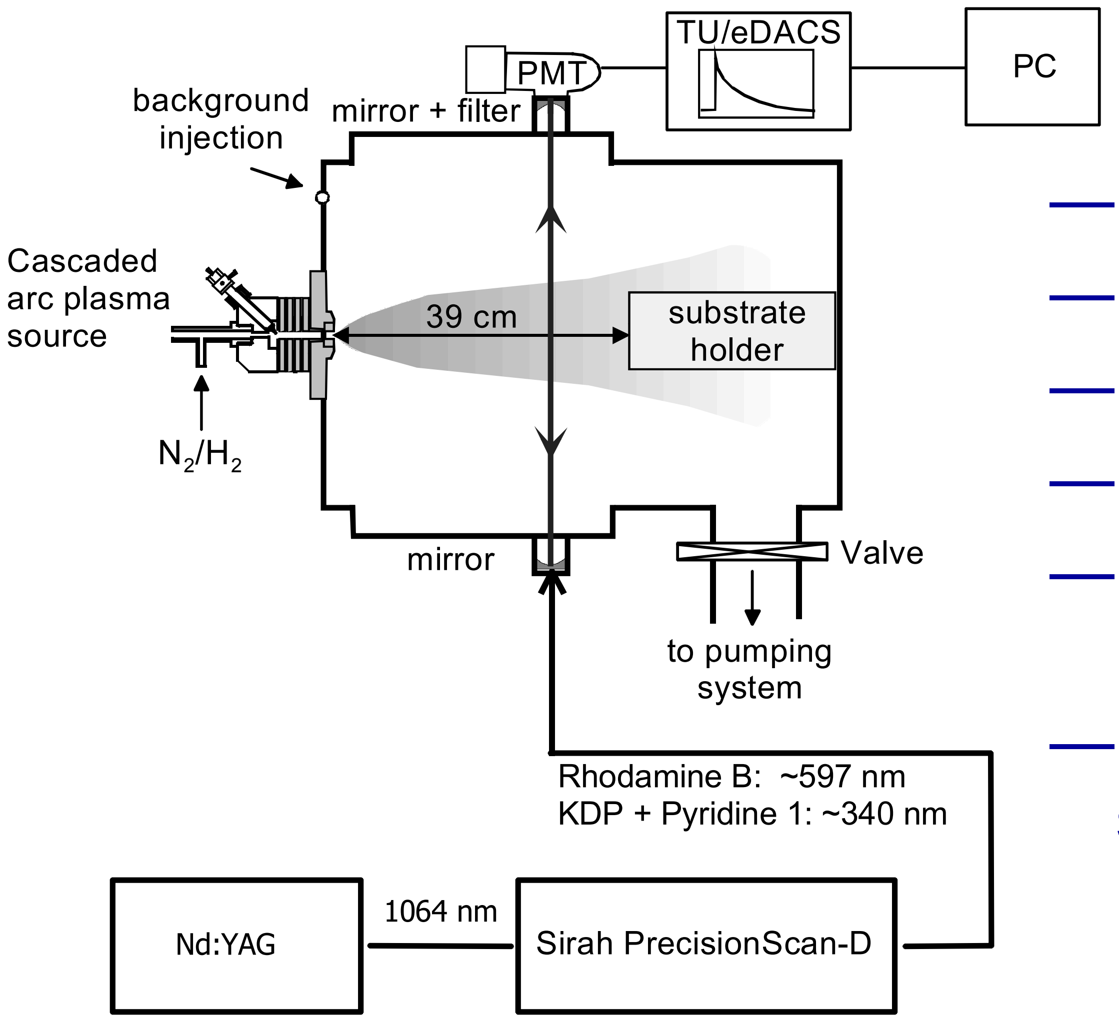
17 sccs N_2/H_2, 20 pa



Role of NH and NH_2 radicals in the ammonia formation

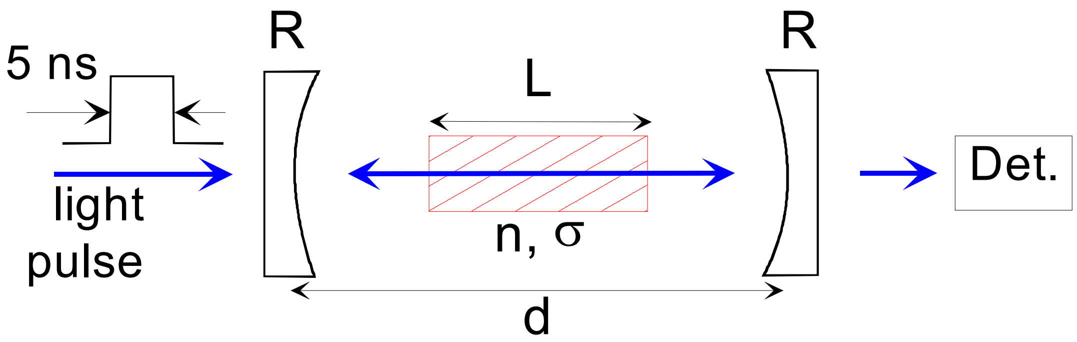
CRDS: Absolute densities

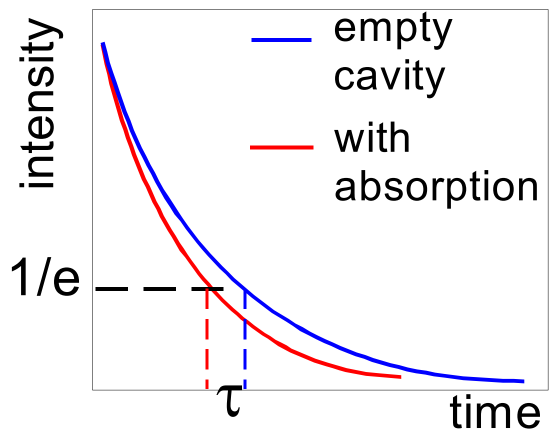
Cavity Ring-Down Spectroscopy system



- Variable measurement position
- Cavity length ~ 112 cm
- Filter to block plasma light
- Small Ar flow to protect mirrors
- Laser power before cavity <100 μJ/pulse
- TU/eDACS: homebuild detection system

Absolute density





- Density in one transition:
  - — Isolated (one single line)
  - — Known absorption cross section

$$n_i = \frac{1}{\sigma L}\left(\frac{d}{c\tau} - \frac{d}{c\tau_0}\right)$$

- Density in all transitions:
  - — Using Boltzmann equation
  - — Known rotational temperature

$$n_{tot} = n_i \frac{\sum_k g_k \cdot \exp\left(\frac{-E_{rot,k}}{kT_{rot}}\right)\exp\left(\frac{-E_{vib,k}}{kT_{vib}}\right)}{g_i \cdot \exp\left(\frac{-E_{rot,i}}{kT_{rot}}\right)\exp\left(\frac{-E_{vib,i}}{kT_{vib}}\right)}$$

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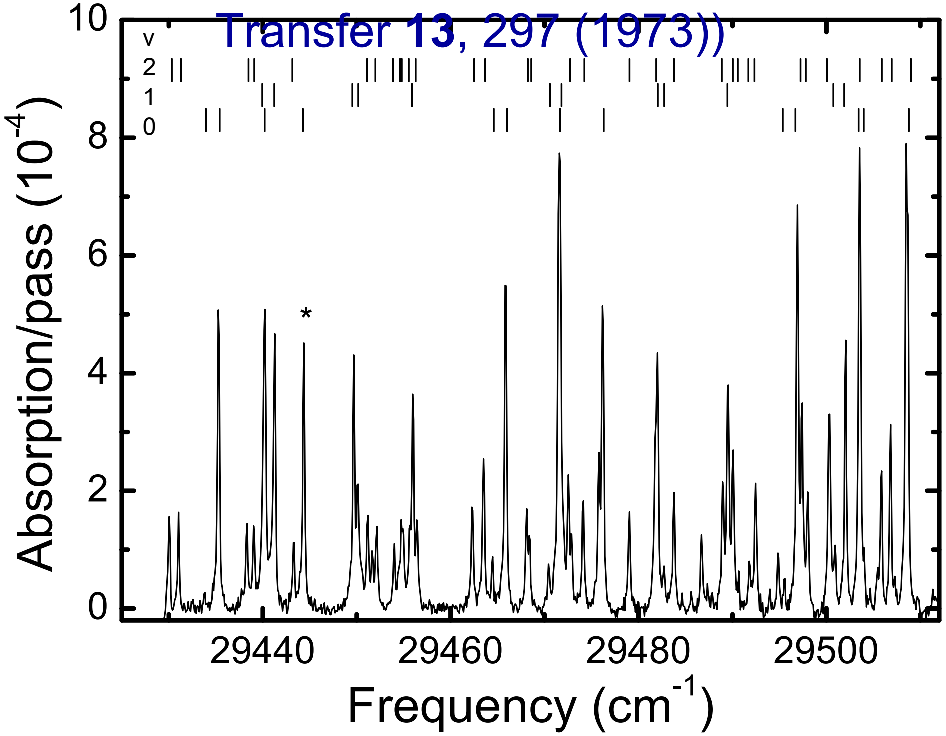
NH and NH_2 spectra

NH

- Pyridine 1: 670 – 712 nm
- KDP: 335 – 356 nm
- UV attenuator
- σ = 2.5 x 10^{-10} m^2Hz

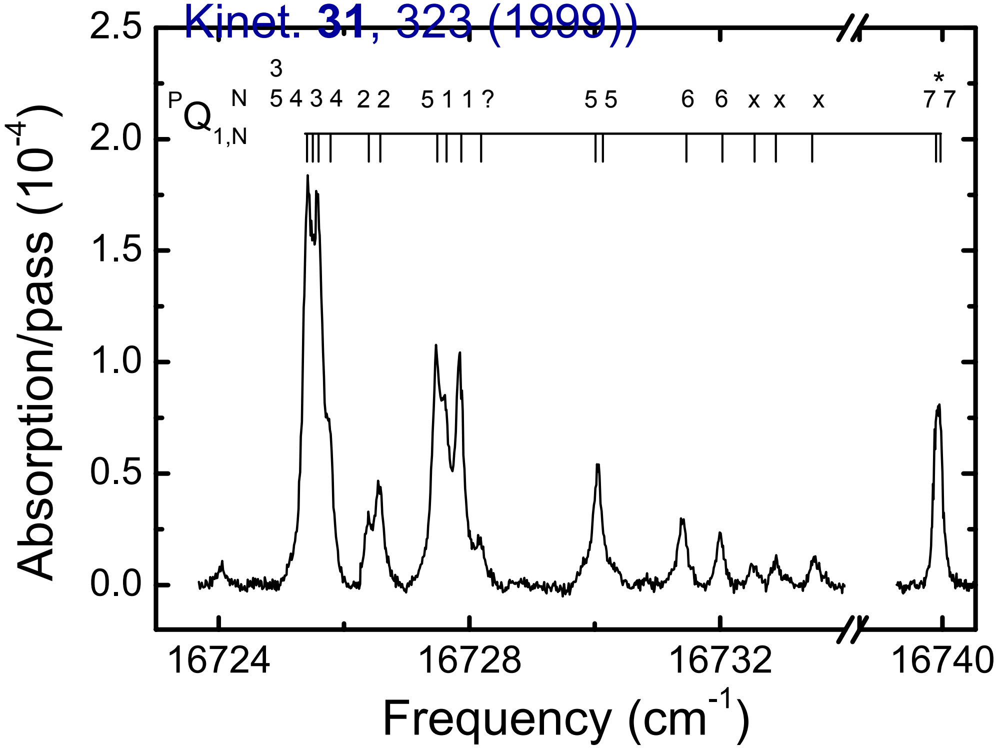
(Lents, J. Quant. Spectrosc. Radiat. Transfer **13**, 297 (1973))



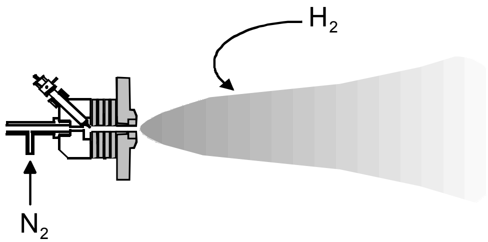
NH_2

- Rhodamine B: 570 – 629 nm
- No amplifier in dye laser
- σ = 2.2 x 10^{-10} m^2Hz

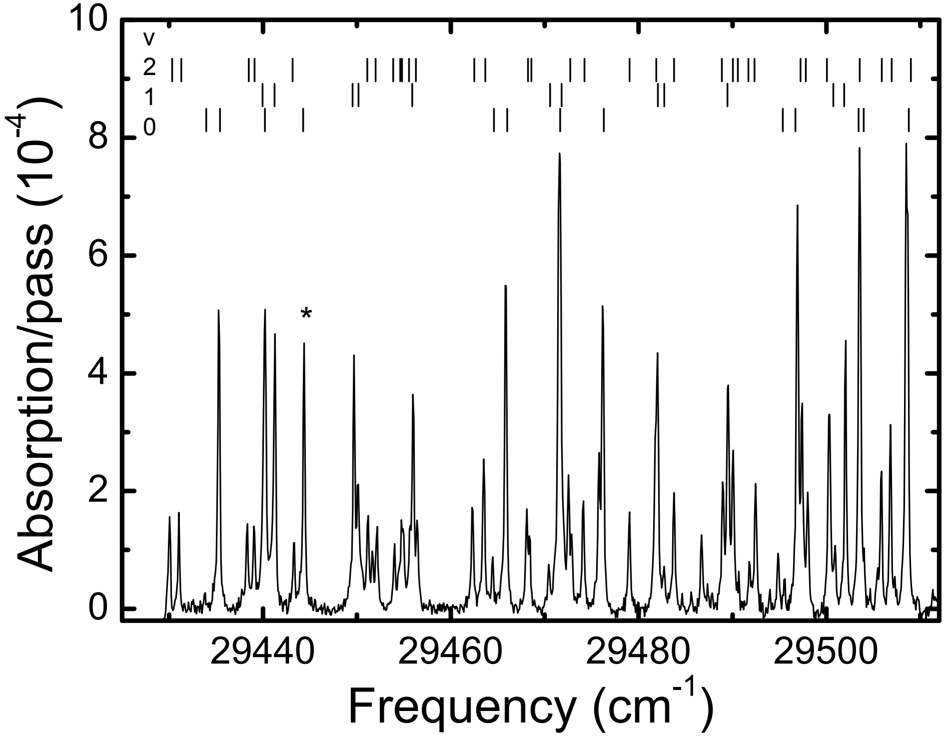
(M. Votsmeier *et al.*, Int. J. of Chem. Kinet. **31**, 323 (1999))

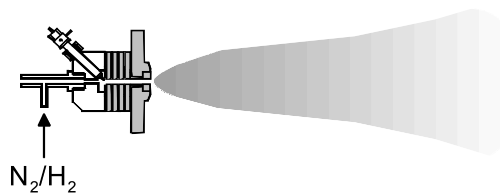


NH spectra @ z = 10 cm in N_2-H_2 plasma

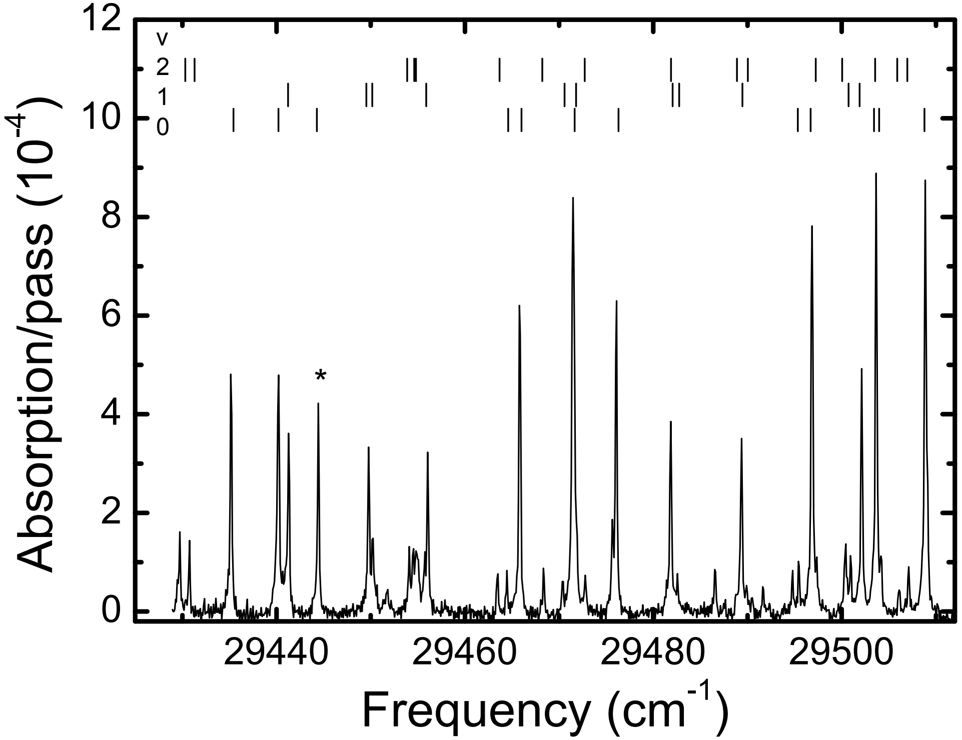


17 sccs N_2, 6 sccs H_2, 20 Pa





5 sccs N_2 12 sccs H_2, 20 Pa

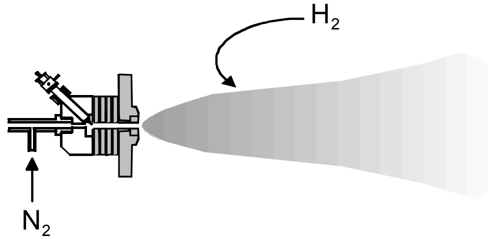


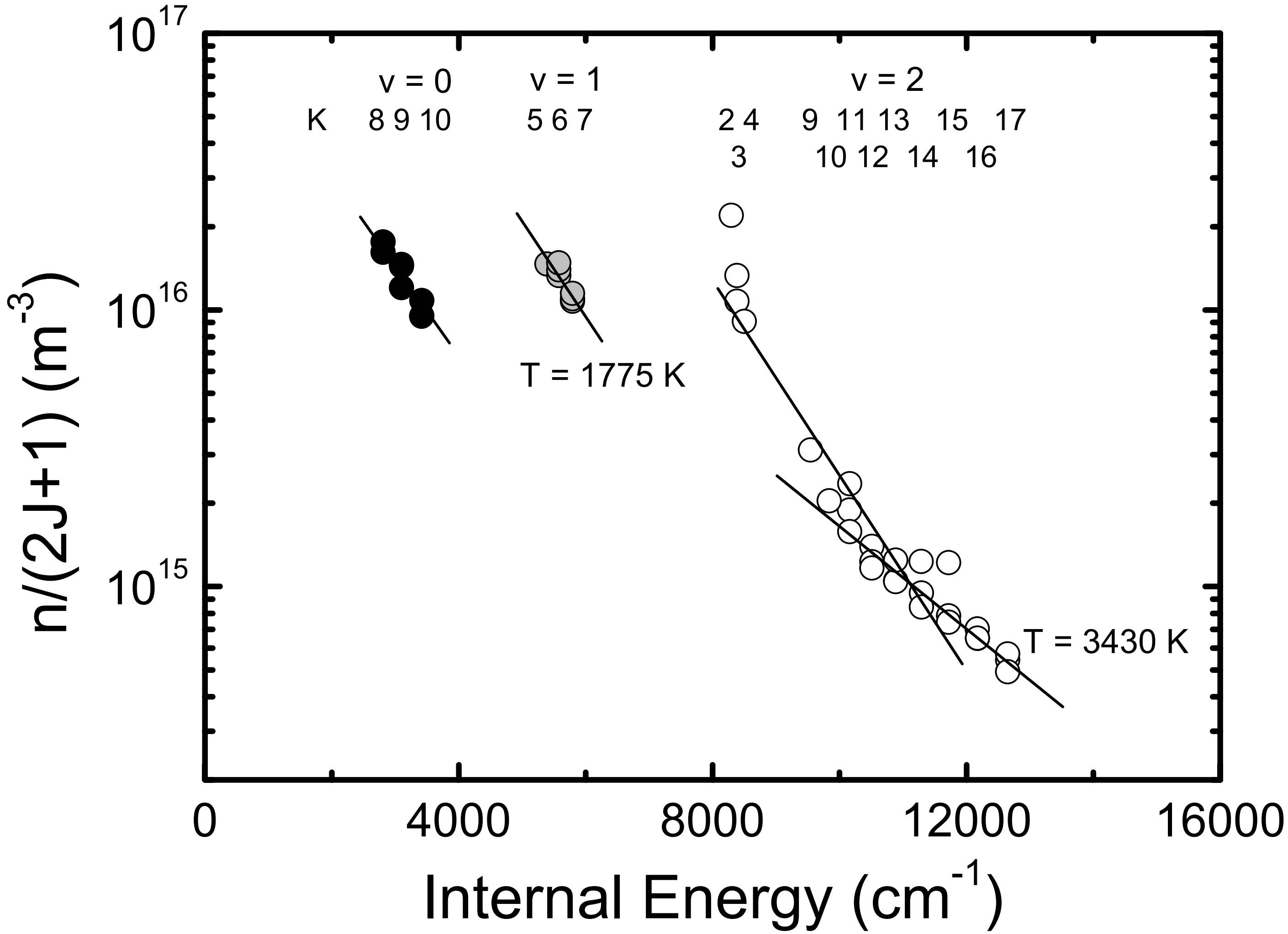
Different spectra → Different plasma chemistry

Rotational density distribution

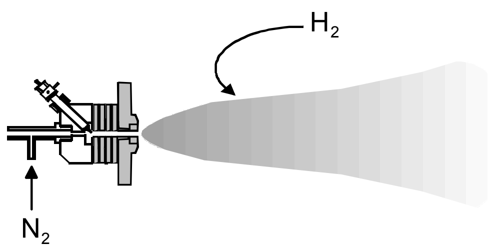
Boltzmann plot @ z = 10 cm

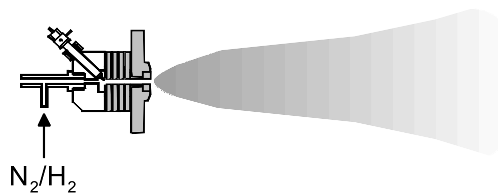
For v =2, K> 12: $T_{rot} > T_{kin}$





Rotational density distribution

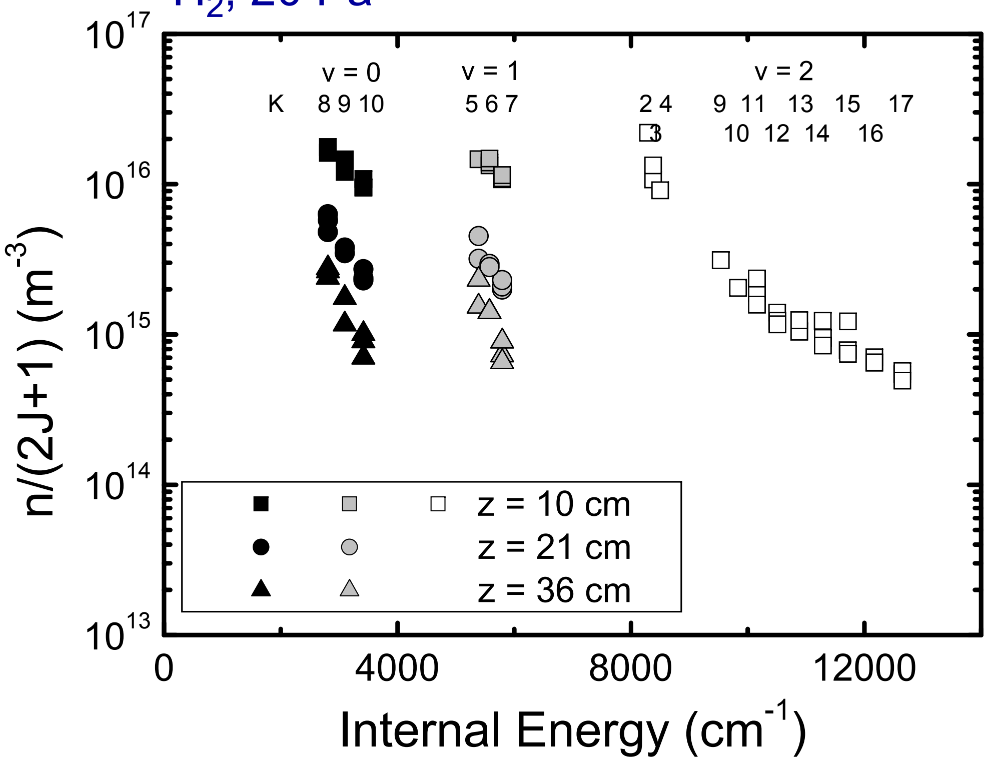


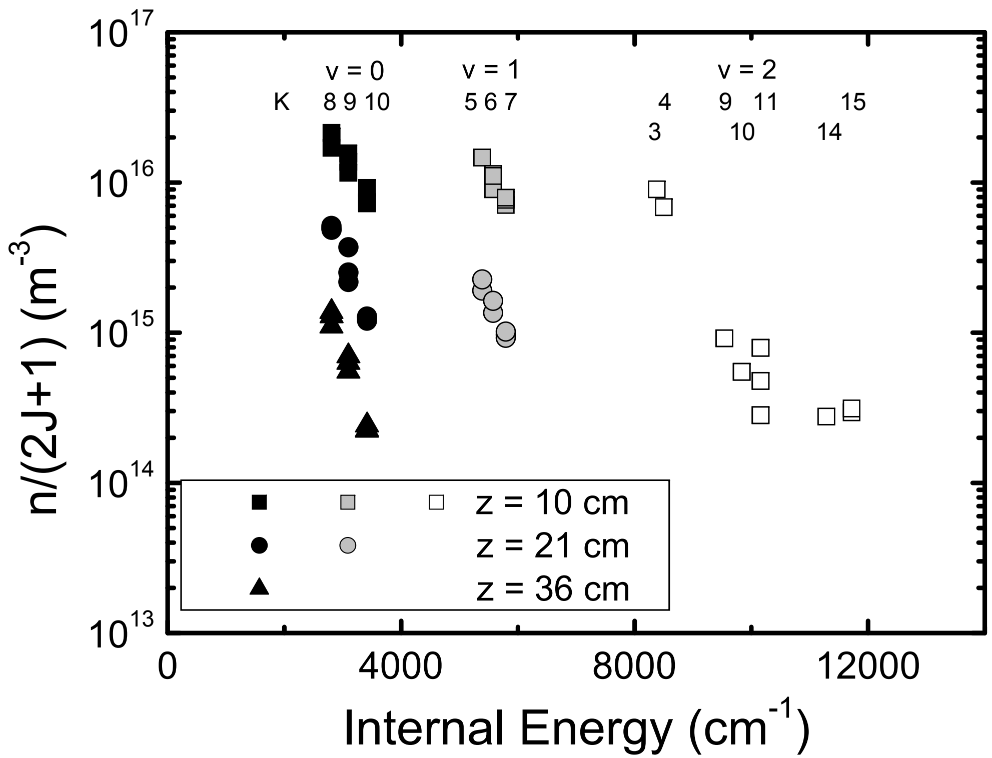


17 sccs N_2, 6 sccs H_2, 20 Pa

5 sccs N_2 12 sccs

H_2, 20 Pa





$T_{rot} \approx T_{kin}$, Vibrational distribution $\neq$ Boltzmann distribution

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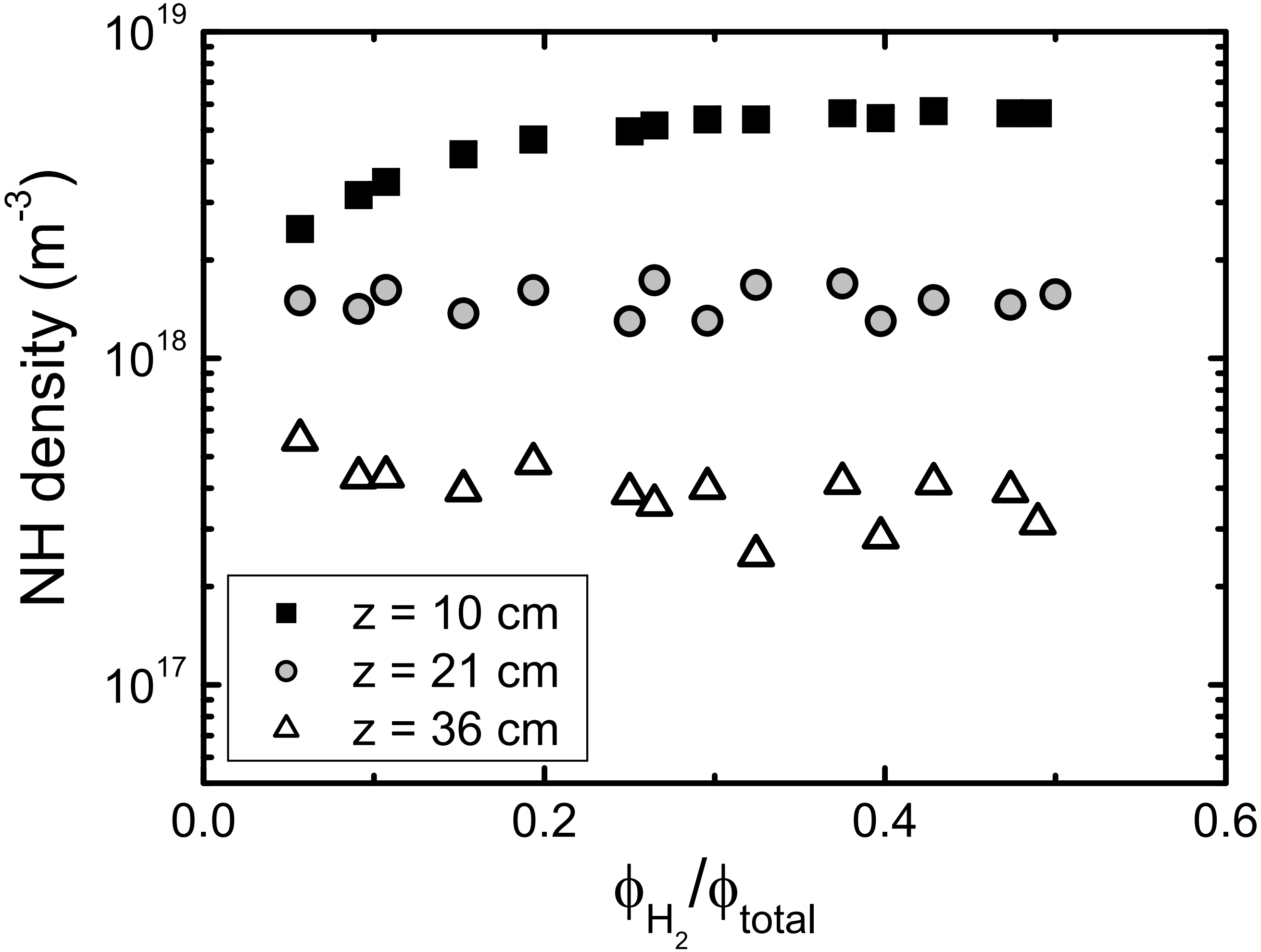
N_2 plasma with H_2 injected in background

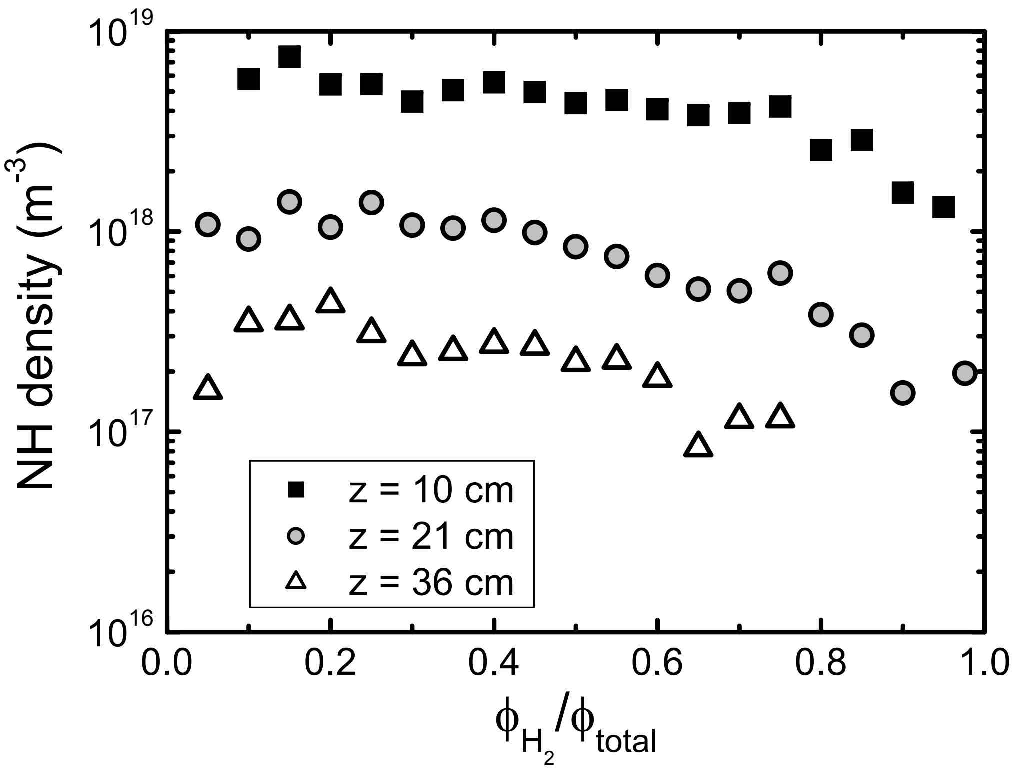


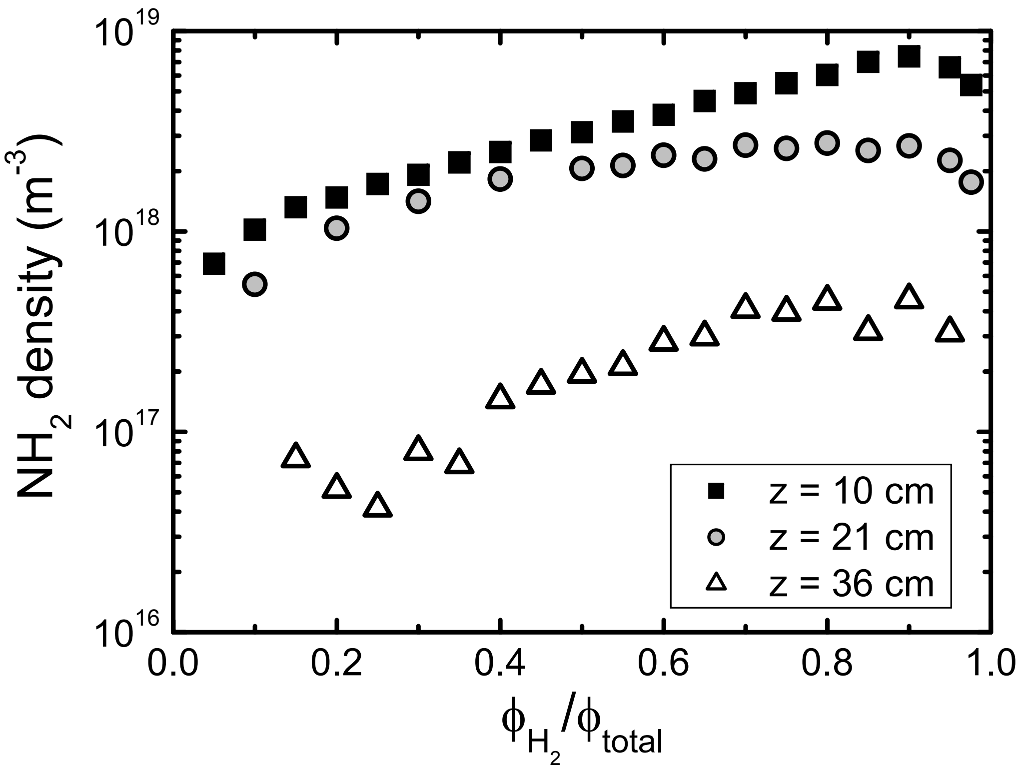
NH

- $N \approx 5 \times 10^{18}\ m^{-3}$
- Gradual increase
- Density saturates for $\phi_{H2}/\phi_{total} > 0.2$

- No NH_2 detected ($n < 3 \times 10^{16}\ m^{-3}$)

Expanding N_2-H_2 plasma





NH

— N ≈ 5 x 10^{18}

— Gradual decrease

— No density saturation

NH_2

— N ≈ 7 x 10^{18}

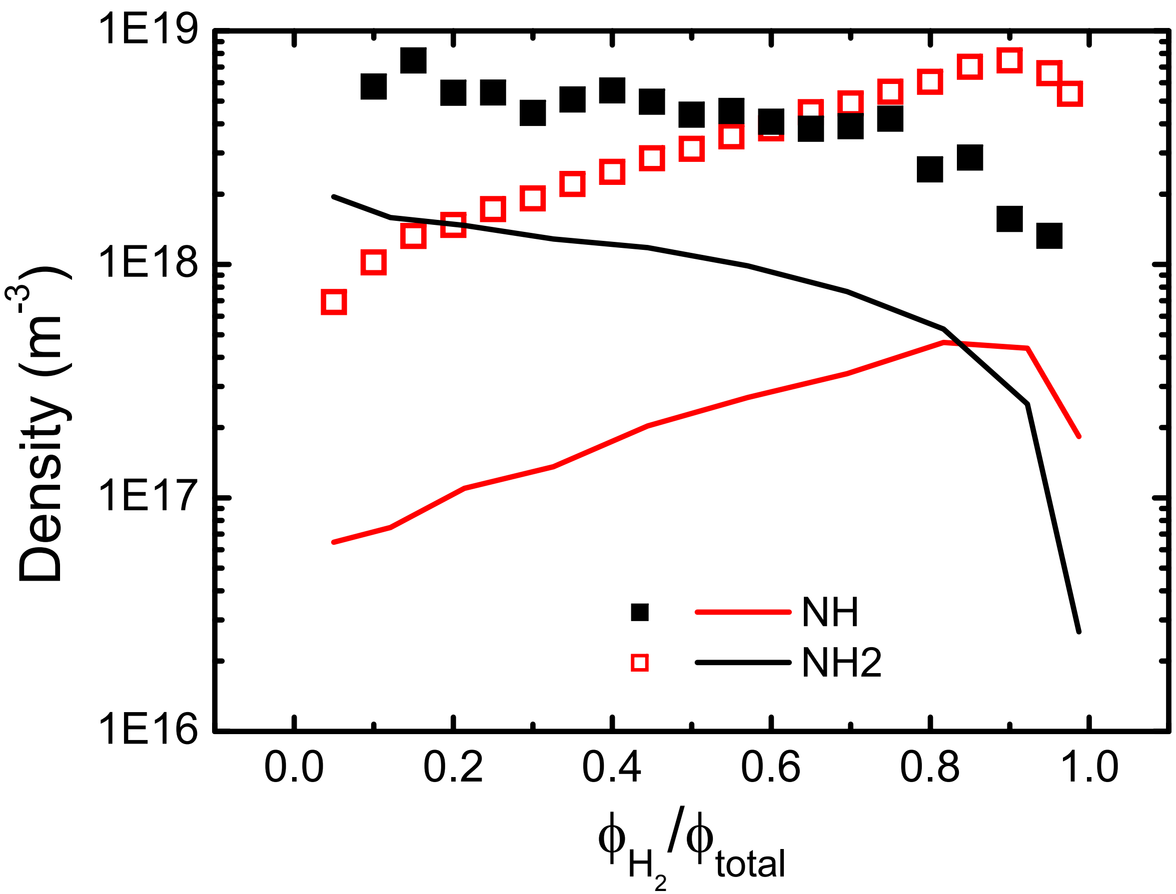
— Gradual increase

Plasma chemistry

Suggested chemistry:

Reactants		Products	k ($m^3 s^{-1}$)
$N^+ + NH_3$	→	$N + NH_3^+$	2×10^{-15}
	→	$HN_2^+ + H_2$	2.2×10^{-16}
	→	$H_2N^+ + NH$	2.2×10^{-16}
$N^+ + H_2$	→	$NH^+ + H$	5.4×10^{-16}
	→	$NH + H^+$	5×10^{-16}
$NH_3^+ + e$	→	$NH_2 + H$	3.6×10^{-14}
	→	$NH + 2H$	1.4×10^{-13}
$NH^+ + e$	→	$N + H$	2×10^{-13}
$HN_2^+ + e$	→	$NH + N$	2.6×10^{-14}
	→	$H + N_2$	1.4×10^{-14}
$H_2N^+ + e$	→	$H_2 + N$	2×10^{-13}
$N + H_2$	→	$NH + H$	$3.8 \times 10^{-16} \exp(-15775/T)$
$NH + H$	→	$N + H_2$	$8.3 \times 10^{-17} \exp(-1000/T)$
$NH + N$	→	$N_2 + H$	$1.8 \times 10^{-17} (T/300)^{0.5}$
$NH + NH$	→	$N_2 + 2H$	8.5×10^{-17}
$NH + NH$	→	$N + NH_2$	$1.7 \times 10^{-18} (T/300)^{0.5}$
$NH_2 + H$	→	$NH + H_2$	2.3×10^{-17}
$N + NH_2$	→	$N_2 + 2H$	1.2×10^{-16}
$NH + NH_2$	→	$NH_3 + N$	1.7×10^{-17}
$NH_3 + H$	→	$NH_2 + H_2$	$9 \times 10^{-25} T^{2.4} \exp(-4991/T)$

Plasma chemistry @ z = 10 cm



Plug down model

- Forward chemistry
- speed of beam
- diffusion of particles

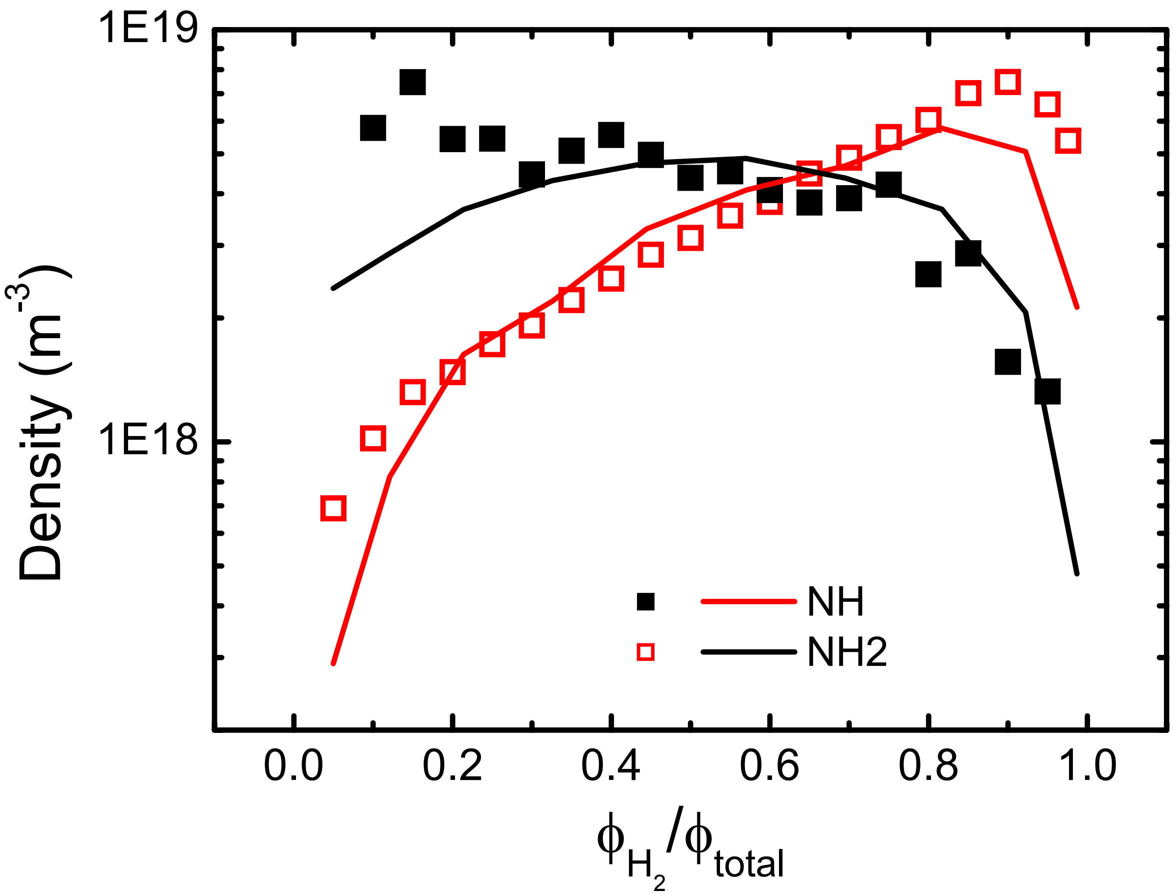
- Factor 10 difference in values
- Reactions producing NH and NH2 are faster:

$N + H_2 \rightarrow NH + N$ $k = 3.8 \times 10^{-16} \exp(-15775/T)\ m^3s^{-1}$

$NH_3 + H \rightarrow NH_2 + H_2$ $k = 9 \times 10^{-25} T^{2.4} \exp(-4991/T)\ m^3s^{-1}$

- In expansion N and H atoms with energy of 0.5 – 1 eV

Plasma chemistry @ z = 10 cm



$N + H_2 \rightarrow NH + H$

$k = 3.8 \times 10^{-16} exp(-7200/T)\ m^3s^-$

$NH_3 + H \rightarrow NH_2 + H_2$

$k = 9 \times 10^{-25} T^{2.4}\ m^3s^{-1}$

$NH_2 + H \rightarrow NH + H_2$

$k = 2.3 \times 10^{-17}\ m^3s^{-1}$

Good agreement experiment and model

— Model reproduces trends

— Factor 2 difference in absolute values

Conclusions

- CRDS can be used in reactive environments
- NH and NH_2 are less than a few percent of NH_3 density
- Flow of NH_x radicals is 2 – 4 sccs
- NH_x radicals are a source for radicals, mainly in the form of N an H atoms at the surface
- High N flows: NH is formed in the plasma beam via N + H_2
- NH_2 is formed via H + NH_3
- High H flows: NH is also formed via H + NH_2

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CENTRUM VOOR PLASMAFYSICA EN STRALINGSTECHNOLOGIE

FOM