On the rotational-translational equilibrium in non-thermal argon plasma at atmospheric pressure

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Motivations

- Neutral gas temperature (T_g) is a primordial parameter in plasma physics

- Crucial in applications such as:
  - treating heat sensitive materials like wood and human tissue
  - fuel synthesis via the dissociation of complex molecules
  - properties of plasma deposited coatings
  - …

- Many techniques to determine T_g:
  - Thermal probes
  - Rayleigh scattering
  - Optical emission spectroscopy (OES)

Motivations

Determination of T_g using OES

- Often relies on determination of a rotational temperature (T_{rot})
  - ➢ Implicitly assumes a rotational-translational equilibrium in the plasma ($T_{rot} = T_g$)

BUT

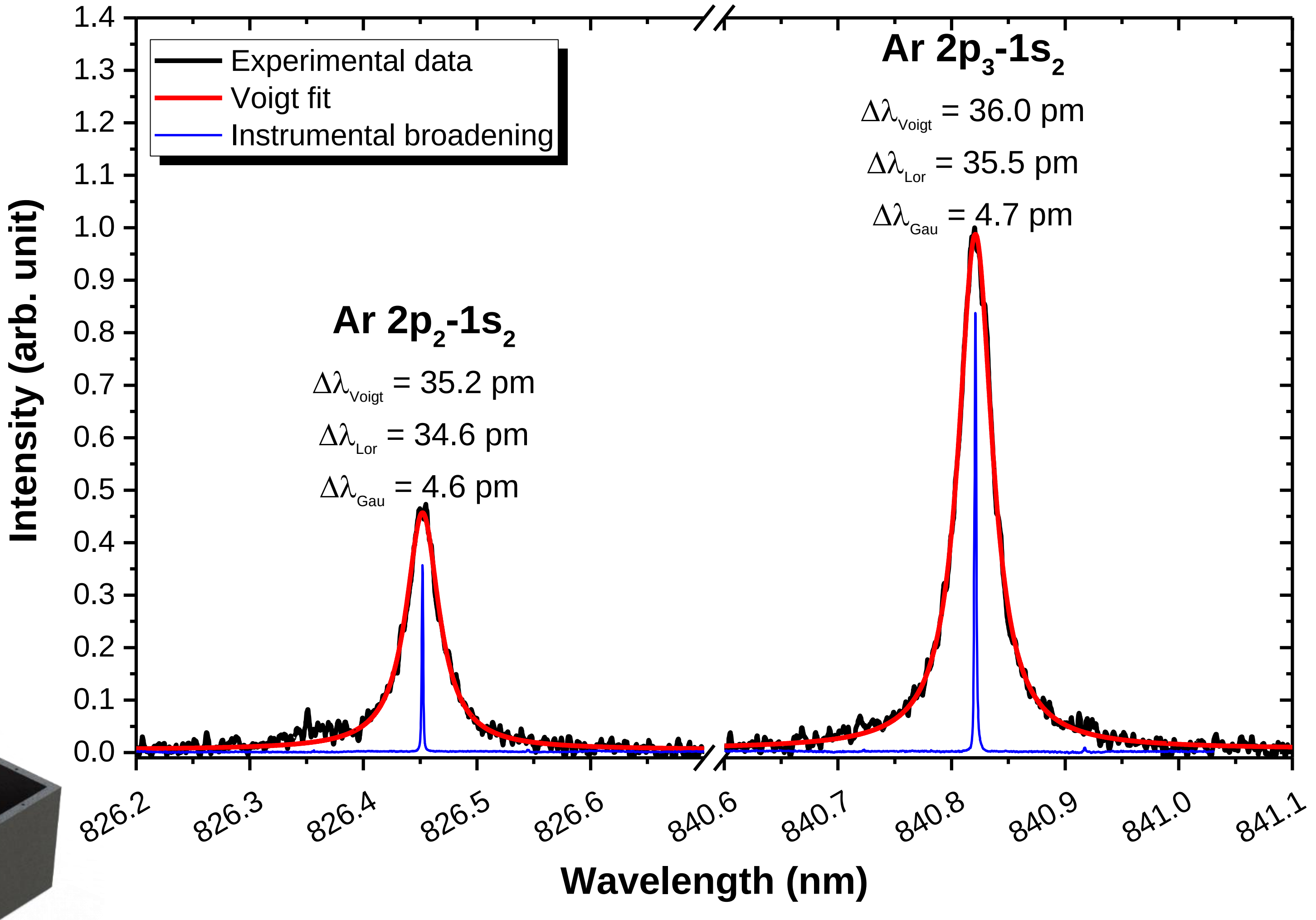
- Needs to satisfy a few criteria to be valid:
  1. The rotational distribution must be thermalized
  2. Energy transfer between rotation and translation is fast enough
  3. No other excitation mechanism of the probed emitting levels alter this thermalization

Aim of this work

Obtain T_g and T_{rot} independently to validate if they can be assumed equal

Data acquisition and analysis: Gas temperature

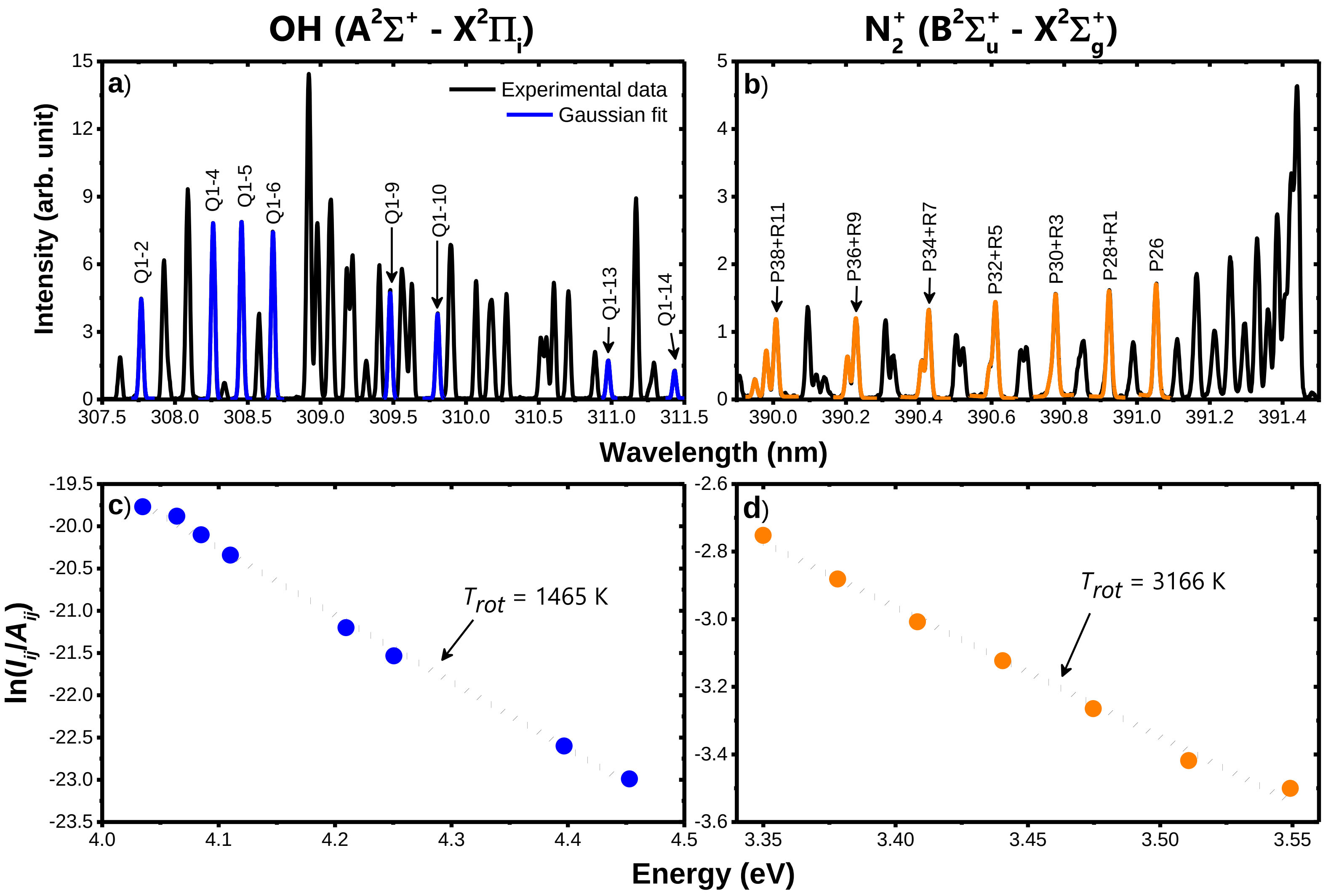
- T_g obtained from the broadening of Ar $2p_2$-$1s_2$ and $2p_3$-$1s_2$ emission lines at $\sim 826\ nm$ and $\sim 841\ nm$
- Strongly affected by resonance and Van der Waals broadening
- Measurements with an ultra-high-resolution spectrometer (LightMachinery HyperFine spectrometer): spectral resolution of 1.8 pm
- $\Delta\lambda_{inst}$ accounts for 5% of the measured line broadening



Data acquisition and analysis: Rotational temperature

- T_{rot} obtained from the rotational structures of OH ($A^2\Sigma^+$- $X^2\Pi_i$) and N_2^+ ($B^2\Sigma_u^+$- $X^2\Sigma_g^+$) systems using the Boltzmann plot method:

$$I_{ij} \propto A_{ij} exp^{\left(\frac{-E_i}{k_B T_{rot}}\right)}$$



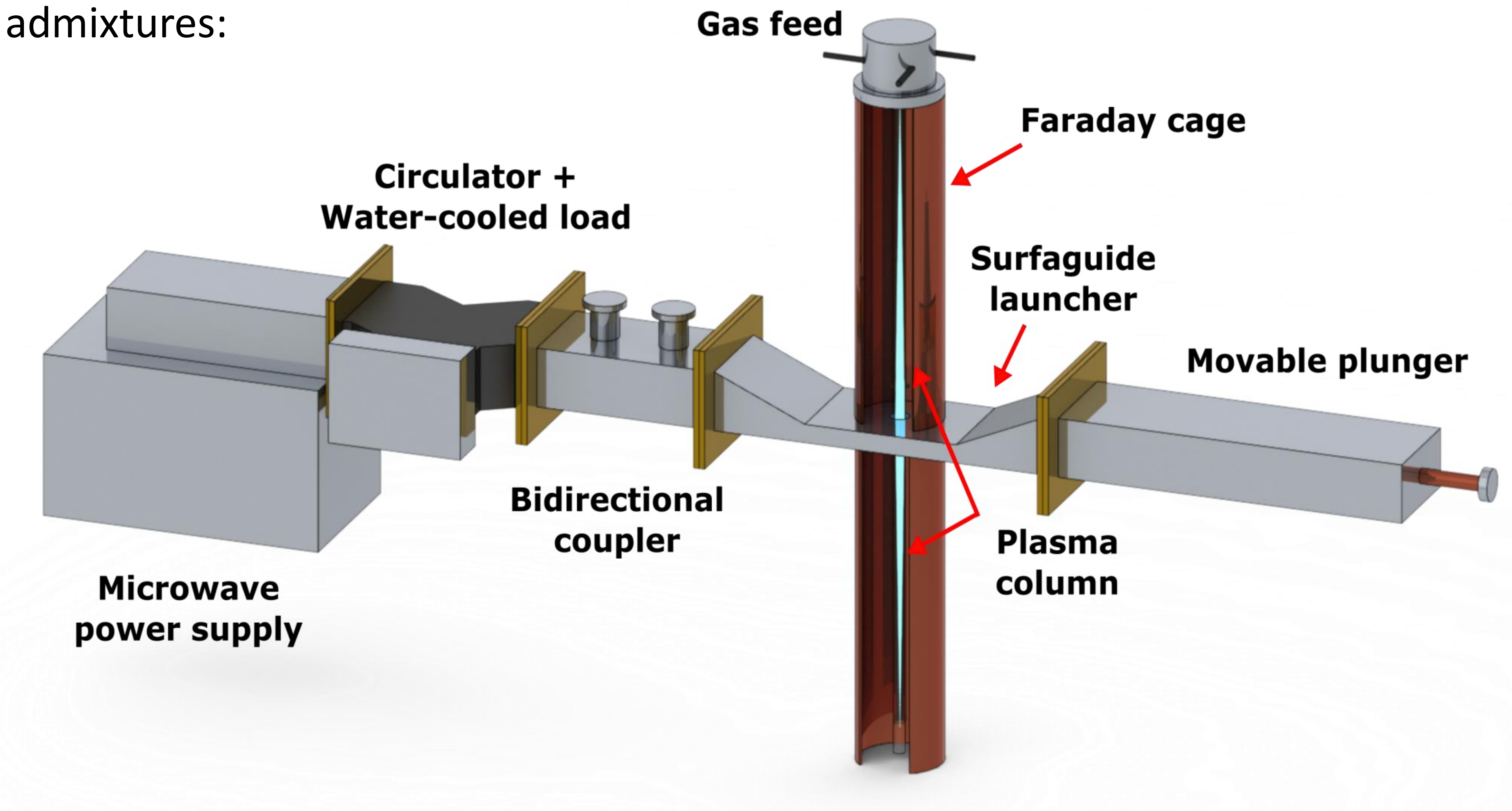
Experimental Setup: Microwave plasma

- Microwave argon plasma at atmospheric pressure
  - Two conditions of admixtures:
    - H_2O traces
    - N_2 (1%)

- 300 W power

- 2450 MHz

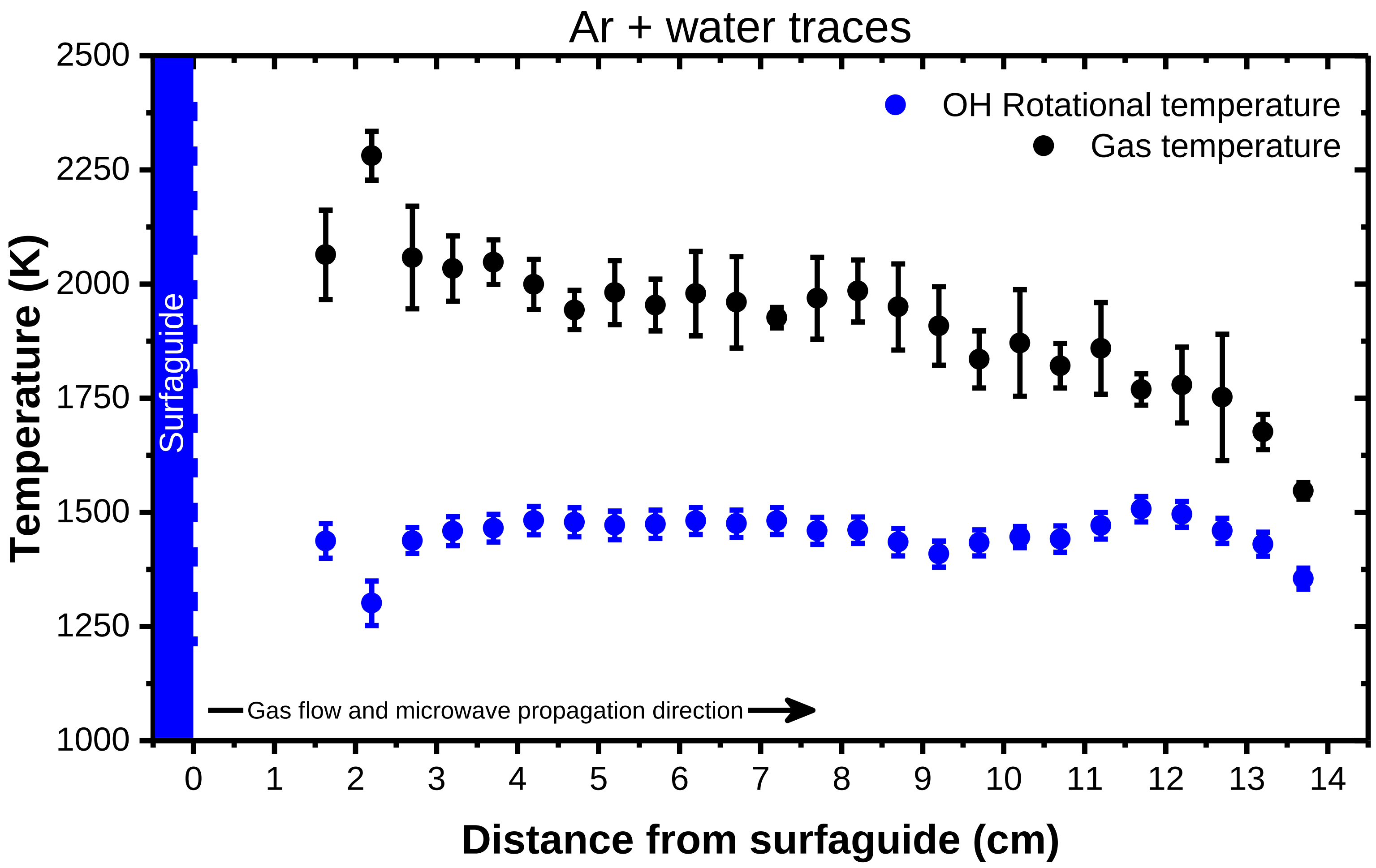
- 500 sccm argon flow



Results: Microwave plasma

Microwave argon plasma with water traces

- T_{rot} mostly constant along the column
- T_g decreases steadily
  - ➢ Decrease of electron number density
- Values and trends all coherent with the literature
- T_{rot} is lower than T_g



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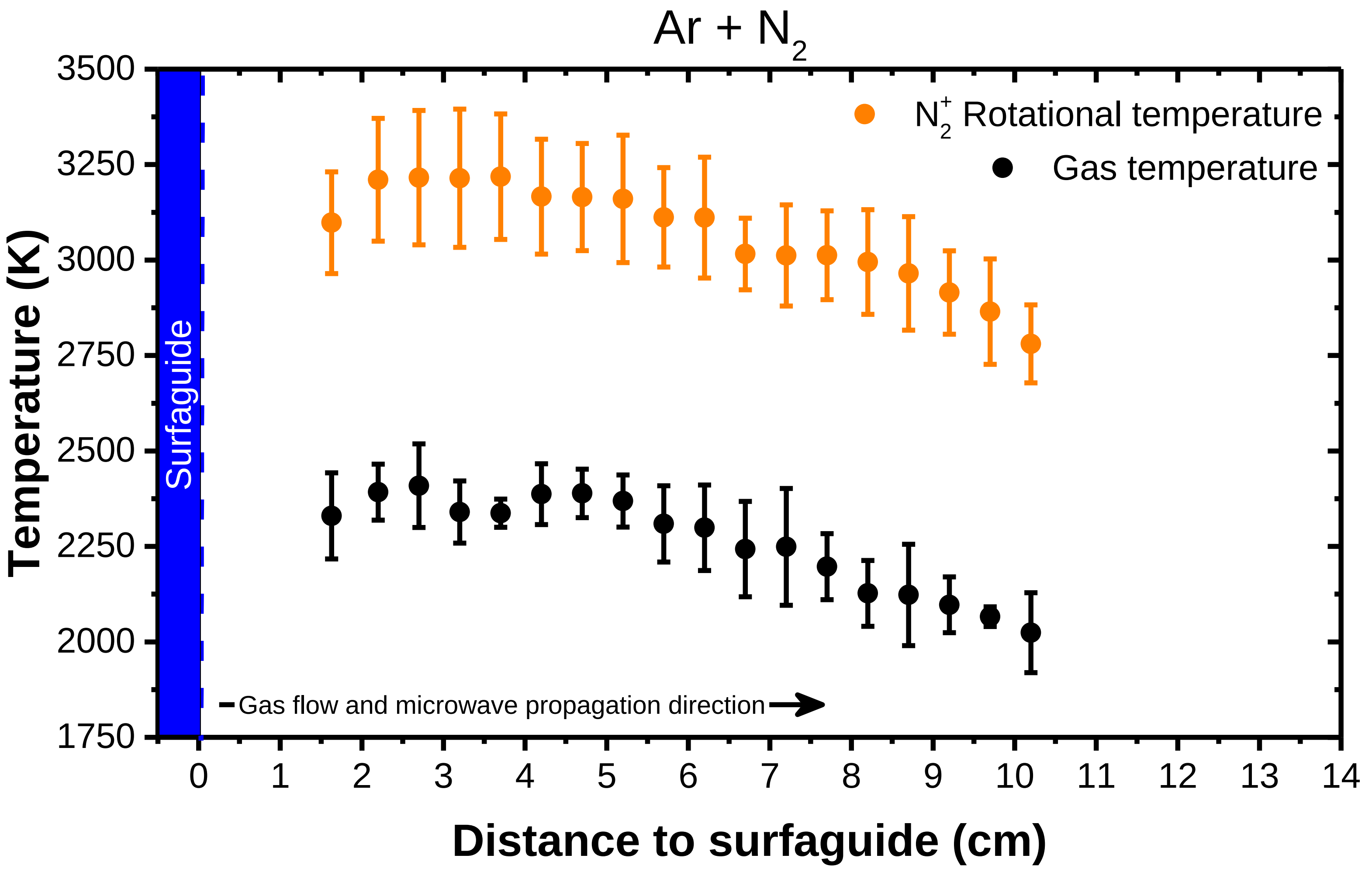
Results: Microwave plasma

Microwave argon plasma with 1% N_2

- Both T_{rot} and T_g values decrease along the column
- Values and trends all coherent with the literature
- T_{rot} higher than T_g



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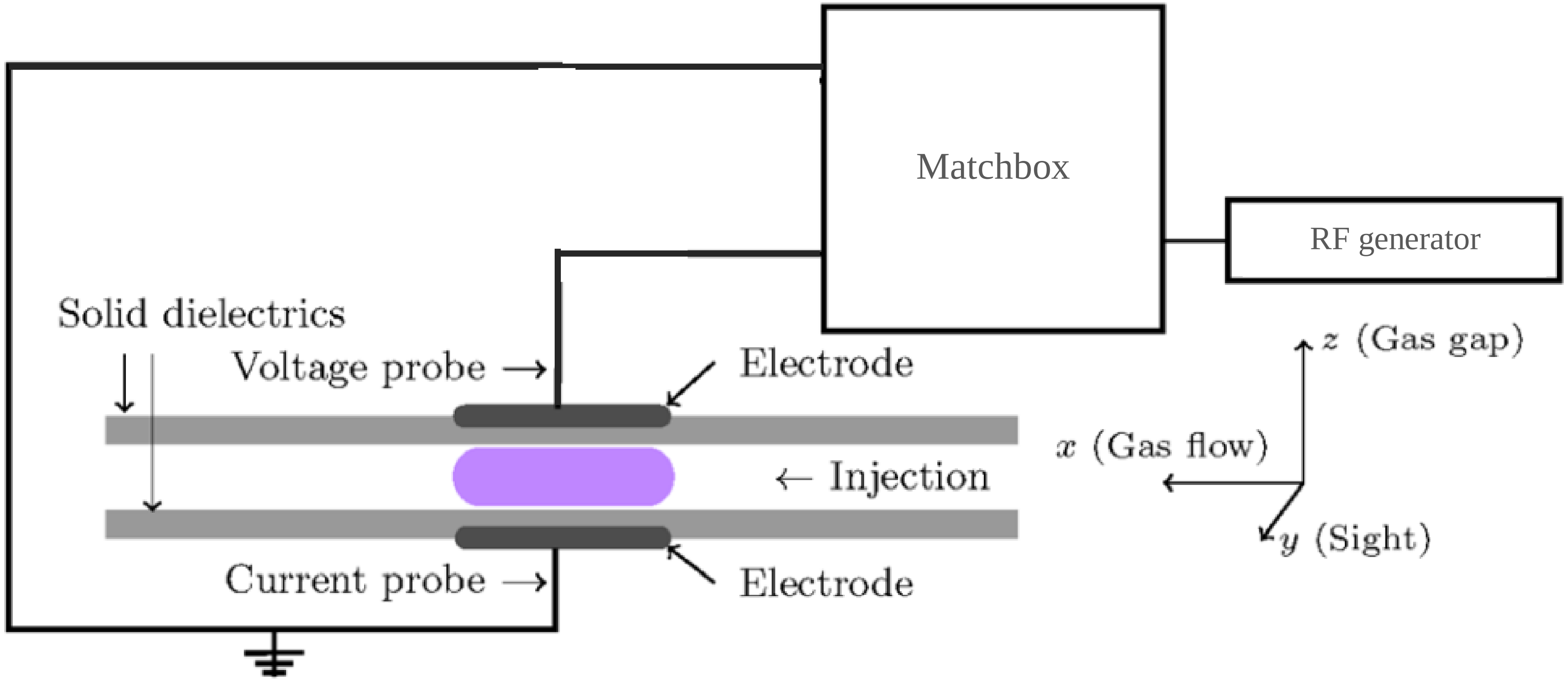
Experimental Setup: Radio-frequency plasma

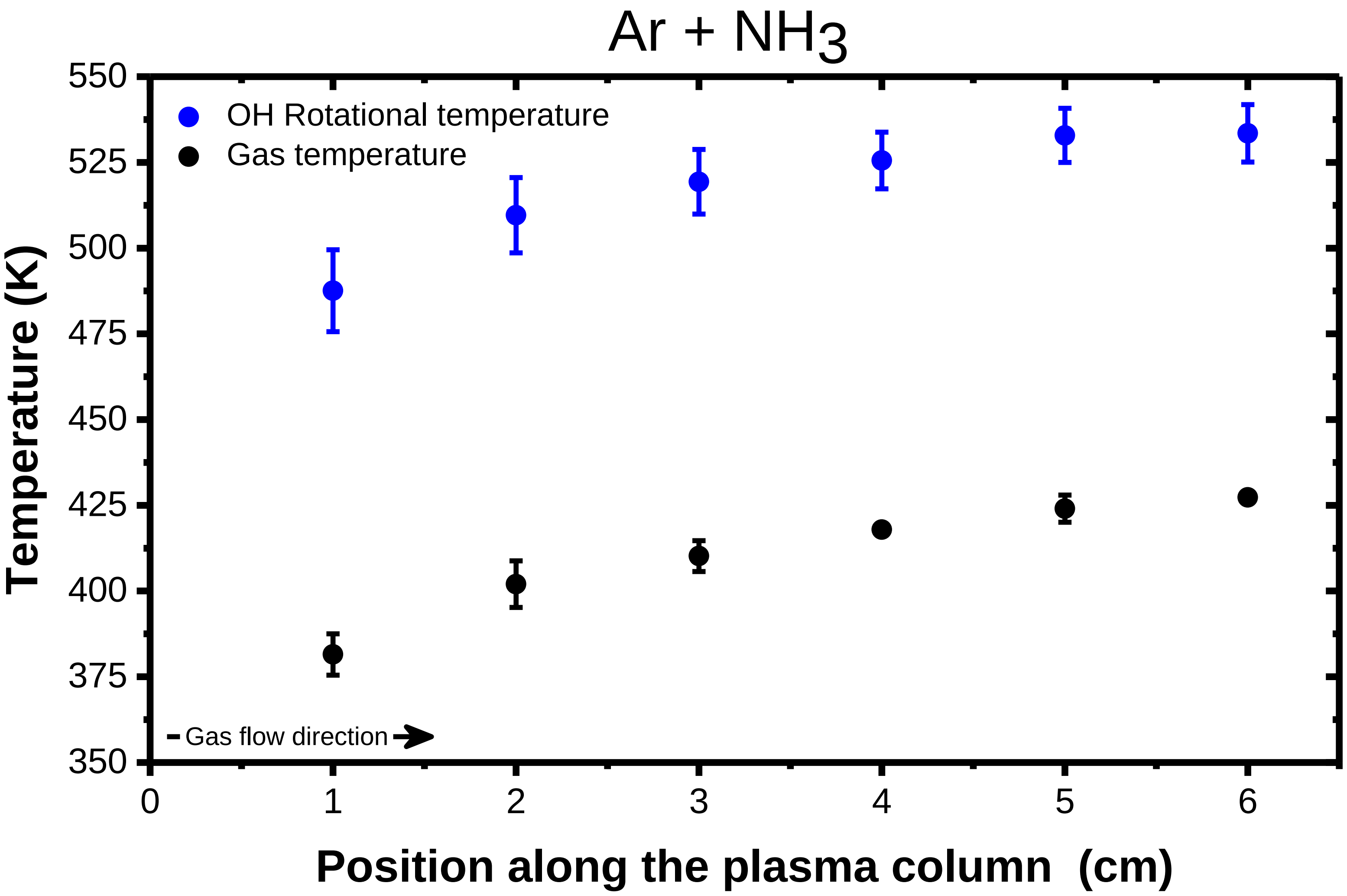
- Capacitively coupled radiofrequency plasma produced at atmospheric pressure
  - ➢ Two linear electrodes (13.56 MHz and grounded)
- 43 W power
- 420 sccm $Ar+NH_3$



Results: Radio-frequency plasma

RF Ar+NH_3 plasma

- T_{rot} and T_g slightly increase
- Values and trends all coherent with the literature
- T_{rot} higher than T_g



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Discussion

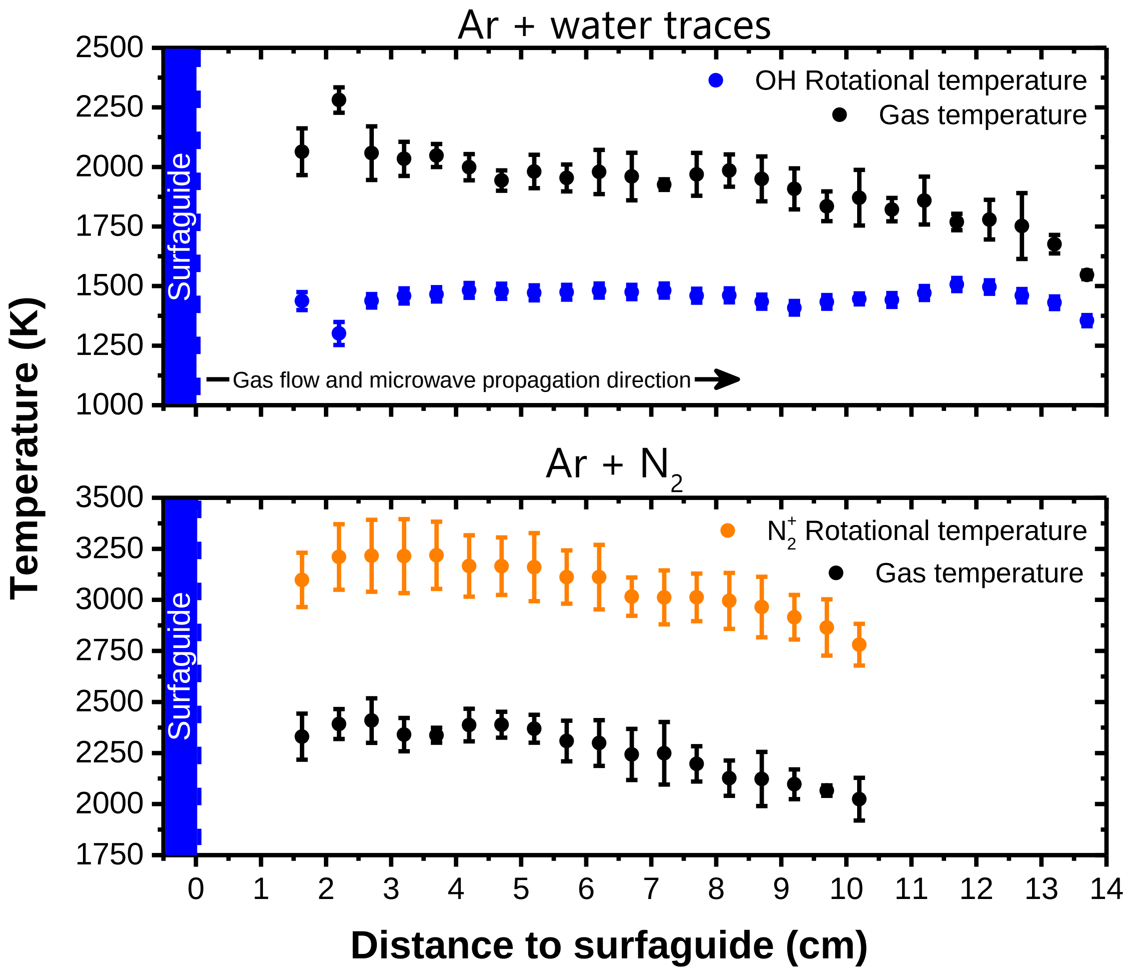
T_{rot} is never equal to T_g

➢ Rotational-translational equilibrium never achieved

Ok… why?

- Instability of OH radicals at gas temperatures higher than $\sim 1800\ K$

- But N_2? RF plasma?

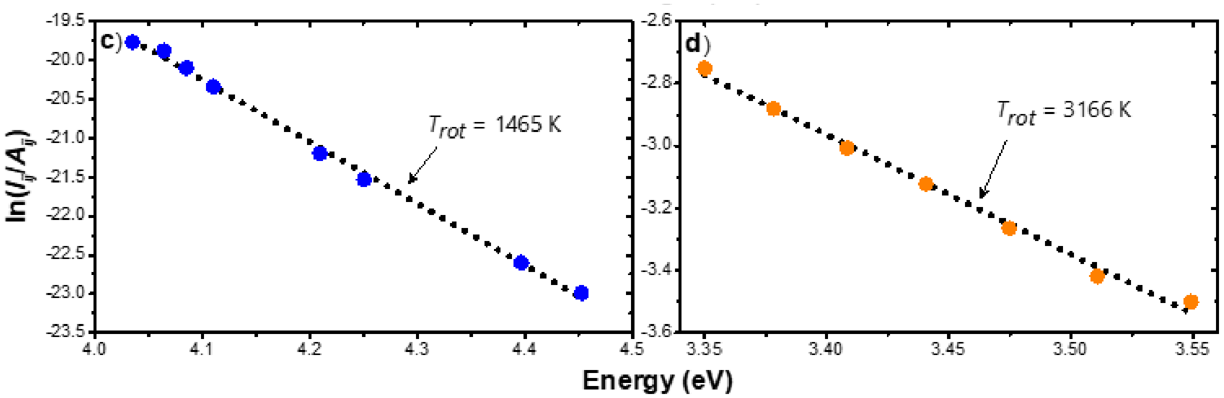


Discussion

Back to basics:

1. Rotational distribution must be thermalized
2. Energy transfer is fast enough
3. No other excitation mechanism

1. The rotational distribution is thermalized ✓



2. The atmospheric pressure ensure a collision frequency between neutral atoms in the 10^9 collisions/s range
   - ➢ Time between subsequent collisions ~10^{-9} s
     - ➢ Average lifetime of excited levels (10^{-10} - 10^{-9} s)
       - ➢ The energy transfer is fast enough ✓

Discussion

3. No other excitation mechanism..?

Air-related molecules are very efficient in quenching Ar metastable states

- Energy close to the excitation energy of OH and N_2^+

A. Durocher-Jean, I. R. Durán, S. Asadollahi, G. Laroche, and L. Stafford, Plasma Process. Polym. e1900229 (2020).
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3. In Ar+N_2 microwave plasma, ~85 % of the total energy transferred to neutral gas heating is from electron-impact excitation
   - Electrons have a high impact on the rotation of molecules = competition of mechanisms

A. Durocher-Jean, N. Delnour, and L. Stafford, J. Phys. D. Appl. Phys. **52**, 475201 (2019).

Other excitation mechanism do exist! ❌

Rotational-translational equilibrium not possible in both plasma conditions

Conclusion

- Distinct spectroscopic diagnostic were used to characterize the rotational-translational equilibrium in non-thermal RF and microwave Ar plasma at atmospheric pressure

- T_{rot} never equaled T_g

- Influence of Ar excited states and electrons on excitation mechanism of emitting levels
  - Rotational-translational equilibrium never found to be verified under studied conditions

$$T_{rot} \neq T_g$$

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Thank you for listening