Investigation of Stark broadening in plasma conversion reactors by means of high resolution optical emission spectroscopy

Arne Meindl[(*)1], Christian K. Kiefer[1], Rodrigo Antunes[1], Ante Hecimovic[1], Ursel Fantz[1,2]

[1] *Max Planck Insitute for Plasma Physics, 85748 Garching, Germany*
[2] *University of Augsburg, 86159 Augsburg, Germany*
[(*)] arne.meindl@ipp.mpg.de

The emergent field of plasma conversion technology aims to convert certain molecules into other more valuable or useful products through volumetric plasma discharges or with the help of plasma-catalytic surface reactions. Some examples of such processes include CO_2 conversion [1,2], CH_4 pyrolysis [3], dry reforming of CH_4 [4], as well as NH_3 synthesis [5]. Microwave-driven plasma reactors allow for volumetric plasma conversion over a wide pressure range up to industrially relevant atmospheric pressures and beyond, where high gas temperatures T_{trans} enable thermal dissociation of the molecules [2]. Figure 1 displays a microwave-driven plasma torch reactor used for CH_4 pyrolysis.

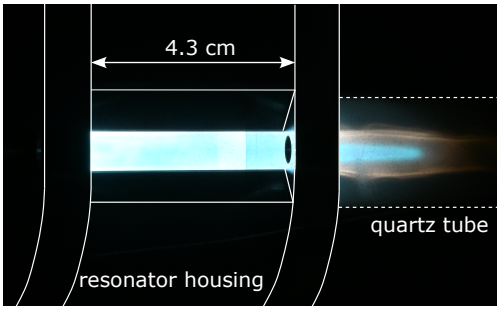

Fig. 1: Microwave-driven plasma torch reactor designed for CH_4 pyrolysis operated at near atmospheric pressure.

An important parameter for understanding the conversion processes is the electron density n_e, since the electrons are delivering the applied energy to the molecules through electron-neutral collisions. This study aims to determine both parameters, T_{trans} and n_e by means of high resolution optical emission spectroscopy of atomic hydrogen emission. T_{trans} is responsible for Doppler broadening of the emission lines, which is of Gaussian shape, while n_e can be determined from Stark broadening, which presents a Lorentzian contribution to the lineshape. A combination of both Gaussian and Lorentzian broadening mechanisms results in an overall lineshape in the form of a Voigt profile.

A high spectral resolution is crucial for precise quantification of the Gaussian and Lorentzian contributions to the lineshapes. For the optical emission spectroscopy (OES) of this investigation, an Echelle spectrometer is used. The spectrometer has a spectral resolution $R = \frac{\lambda}{\Delta\lambda} = 45000$, resulting in instrumental broadenings (FWHM) of $14.6\,\text{pm}$ at $656.3\,\text{nm}$ (H_α) and $10.8\,\text{pm}$ at $486.1\,\text{nm}$ (H_β). Moreover, it enables single-exposure detection of the spectral range from $240\,\text{nm}$ to $880\,\text{nm}$, thus covering the entire Balmer series of atomic hydrogen emission.

For the analysis of the detected spectral lines, lineshape models for H_α and H_β emission have been implemented. In order to approximate the overall lineshape of the atomic hydrogen emission, the hyperfine structure of the atomic hydrogen emission is considered. Figure 2 shows a breakdown of the different hyperfine structure components and the overall resulting profile of H_α emission. For approximation of each of the transitions, Voigt profiles are used, summing up to a resulting profile, which then corresponds to the profiles detected via OES.

The lineshape modeling is further complicated by additional broadening mechanisms that have to be considered. Besides Stark and Doppler broadening, the emission lines are subject to natural line broadening, instrumental broadening, Van-der-Waals broadening, and potentially resonance broadening [6]. Instrumental and Doppler broadening are Gaussian in shape, while the other mechanisms result in Lorentzian shaped broadening contributions. The lineshape model is applied to the measurement via a fitting algorithm. In the first instance, this results in a precise determination of the overall Gaussian and

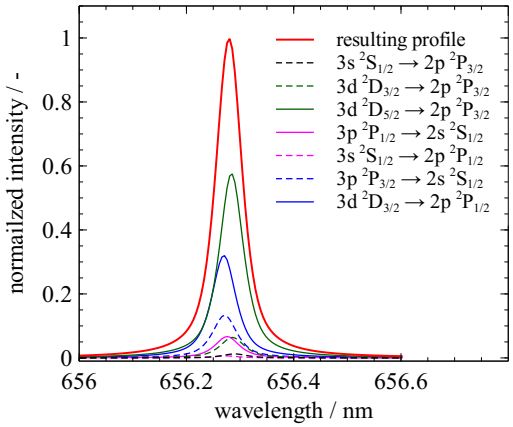

Fig. 2: Contributions of different hyperfine structure components to the overall lineshape of H_α for $T_{trans} = 2100\,\mathrm{K}$ and $n_e = 8 \times 10^{19}\mathrm{m}^{-3}$. Each transition is modeled using a Voigt profile.

Lorentzian components of the Voigt profiles. Knowing the instrumental broadening, the gas temperature T_{trans} can be determined directly from the Doppler contribution to the Gaussian width. Differentiating between the different Lorentzian contributions is more challenging and requires quantification of the other Lorentzian broadening mechanisms in order to determine the Stark contribution and ultimately n_{e} [7,8].

Figure 3 shows an example of an OES measurement taken in the resonator section of a CH_4 microwave discharge (see Fig. 1). The electron density n_{e} and gas temperature T_{trans} are determined using a lineshape model accounting for the hyperfine structure as well as natural, instrumental, Doppler, Van-der-Waals, and Stark broadening.

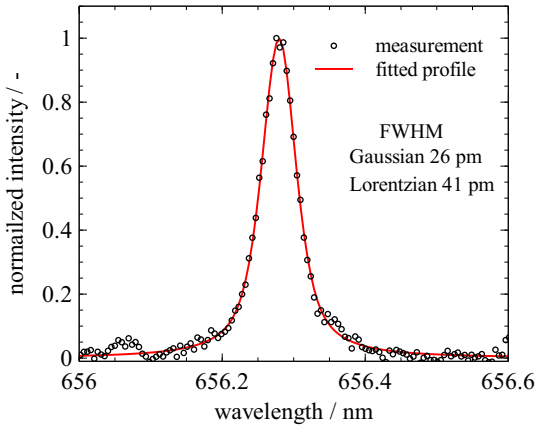

Fig. 3: High resolution measurement of H_α emission in a CH_4 microwave discharge at 100 mbar with lineshape fit resulting in $T_{\mathrm{trans}} = 2100\,\mathrm{K}$ and $n_{\mathrm{e}} = 8 \times 10^{19}\mathrm{m}^{-3}$.

[1] R. Snoeckx et al., *Chem. Soc. Rev.* **46** (2017) 5805–5863.
[2] A. Hecimovic et al., *Journal of CO_2 Utilization* **71** (2023) 102473.
[3] S. Kreuznacht et al., *Plasma Processes and Polymers* **20** (2023) 2200132
[4] S. Kelly et al., *Journal of CO_2 Utilization* **75** (2023) 102564.
[5] P. Navascués et al., *ACS Sustainable Chem. Eng.* **8** (2020) 14855-14866.
[6] A.Y. Nikiforov et al., *PSST* **24** (2015) 034001.
[7] D.E. Kelleher, *J. Quant. Spectrosc. Radiat. Transfer* **25** (1981) pp. 191-220.
[8] P.D.G. Maqueo et al., *J. Phys. D: Appl. Phys.* **51** (2018) 134005.